

Pilot Scale Evaluation of Biological Activated
Carbon for the Removal of THM Precursors

North Texas State Univ., Denton

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PILOT SCALE EVALUATION OF BIOLOGICAL ACTIVATED
CARBON FOR THE REMOVAL OF THM PRECURSORS

by

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16. ABSTRACT This project evaluates a method for the removal of trihalomethane (THM) precursors from surface water sources. A pilot plant was operated for 80 weeks to test the combination of ozone and granular activated carbon (GAC). This combination is sometimes referred to as biological activated carbon (BAC). An important objective was to investigate the possibility of microbiological degradation of THM precursors in the GAC columns and the effect of preozonation on this process. Analysis of the pilot plant data shows microbiological activity to be a significant contributor to the removal of total organic carbon (TOC) and trihalomethane formation potential (THMFP) in GAC columns under the conditions tested. Comparison of costs associated with the addition of GAC and BAC to traditional water treatment plants of 100-, 10-, and 1-mgd capacities shows that, for the conditions of this study, the addition of ozone was not cost effective in extending the time between reactivations of the GAC.		
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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

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ABSTRACT

This report describes research designed to evaluate methods for the removal of trihalomethane (THM) precursors from surface water sources. The site of the project, Cross Lake in Shreveport, Louisiana, is representative of sources that are heavily loaded with THM precursors.

Several treatment processes for precursor control were tested in a pilot plant for 80 weeks. These processes included alum flocculation and mixed-media filtration, ozonation, and granular activated carbon (GAC) filtration. An important objective of the pilot study was to investigate the possibility of microbiological degradation of precursors on GAC columns, and the effect of preozonation on this process.

Water from Cross Lake was pretreated by alum flocculation, tube settling, and mixed-media filtration. The settled-filtered water was split into two streams, one going directly to GAC columns and the other to a turbine-type ozone contactor. Water from the ozone contactor was split into two streams: one was sent directly to GAC columns, and the other was held in a basin for a residence time sufficient to allow dissipation of ozone. Water from the basin was then pumped to GAC columns. For each of the three streams described above, GAC treatment consisted of downflow filtration through two tandem stainless steel columns with 4 feet of Filtrasorb-400 carbon. Empty bed contact time (EBCT) in each GAC filter was 12 minutes at 2 GPM with a hydraulic loading of 2.5 G/ft.²-min. Total EBCT for each GAC train was 24 minutes. Water samples were taken after each treatment step and tested for total organic carbon (TOC), trihalomethane formation potential (THMFP), inorganic carbon (INC), modified total plate counts, ATP, and other parameters. Analysis of the pilot plant data indicates microbiological degradation to be a significant contributor to removal of TOC and THMFP in GAC columns under the conditions tested. In the initial stages the removal mechanism appears to be primarily adsorption. After 50×10^3 bed volumes have been processed, only microbiological processes prevail. During the interim period both adsorption and microbial processes appear to contribute to THMFP and TOC removal.

An analysis of costs associated with the addition of GAC to traditional water treatment plants of 100, 10 and 1 MGD capacities shows that extended lifetimes of the columns lead to cost projections in the range of \$0.13 to \$0.33 /K gallon.

Parallel studies at the Shreveport Amiss plant show high levels of THM's. Alternatives for lowering the levels to less than 0.10 mg/L

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include addition of GAC columns and conversion to chloramination. An alternative oxidant will probably be required in either case for manganese control.

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LIST OF ABBREVIATIONS, SYMBOLS AND UNIT CONVERSIONS

ABBREVIATIONS AND SYMBOLS

GAC	--	granular activated carbon
BAC	--	biological activated carbon
THM	--	trihalomethane
TOX	--	total organic halogen
MTPC	--	modified total plate count
ATP	--	adenosine triphosphate
LLE	--	liquid-liquid extraction
EBCT	--	empty bed contact time
SEA	--	soil extract agar
O ₃	--	ozone
THMFP	--	trihalomethane formation potential
TOC	--	total organic carbon
INC	--	inorganic carbon

CONVERSIONS TO METRIC EQUIVALENTS

G	gallon	(3.785 liters)
GPM	gallon/minute	(0.2271 m ³ /hr)
gal/ft ² -min	gallon/square foot- minute	(2.445 m/hr)
MGD	1 million gallons/day	(157.7 m ³ /hr)
hp	horse power	(0.745 kilowatt)
ft	foot	(0.3048 meter)
lb	pound	0.454 kg
lb/ft ³	pounds/cubic foot	(16.02 kg/m ³)
lb/in ²	pounds/square in (psi)	6895 Pascals

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SECTION 1

INTRODUCTION

Following the passage of the Safe Drinking Water Act by the U.S. Congress in 1974, the U.S. Environmental Protection Agency (EPA) proceeded to act under the authority of this legislation to promulgate National Interim Primary Drinking Water Standards. These standards set maximum contaminant limits for several inorganic elements and compounds, organic pesticides, radioactivity levels, and microbiological parameters. They were applied to essentially all water supplies serving populations in the United States. More recently, these standards have been amended to include the establishment of maximum contaminant levels for four organic substances known as the trihalomethanes (THM's). Trihalomethanes are known to be formed by the disinfection process that uses chlorine, the disinfectant most commonly used in the United States. Research has established that the reaction of chlorine with naturally occurring organic compounds called THM precursors results in the formation of a variety of chlorinated organic compounds, including the THM's. Four THM's are now regulated by the requirements of the Safe Drinking Water Act -- chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. The combined concentrations of these four THM's must not exceed 0.10 mg/L in water supplies serving more than 75,000 persons as of November 29, 1981, and those water systems serving between 10,000 and 75,000 persons as of November 29, 1983. Trihalomethane limits are expected to be extended to cover nearly all U.S. water supplies in the future.

Methods for the control of THM levels include modification of the disinfection process (including substitution of an alternative disinfectant), the removal of THM's once formed by advanced treatment processes such as adsorption and aeration; and the removal of THM precursors before the use of chlorine as a disinfectant. Among the treatment methods available for the removal of THM precursors, granular activated carbon (GAC) adsorption has emerged as the most promising alternative. Various studies have shown that GAC can remove natural organic compounds from groundwaters and surface waters with great efficiency. The principal disadvantage of the use of GAC is the need to replace or reactivate it periodically to renew its adsorption capabilities. This process is a relatively expensive one that has discouraged the wide application of granular activated carbon as a water treatment process. A recent discovery suggests the possibility of extending the lifetime of GAC columns for water treatment. This discovery involves the recognition that microbiological processes occur on GAC in much the same way that they occur in trickling filters for wastewater treatment. Bacterial colonies

have been known to proliferate on GAC for some time, but only recently has it been appreciated that this presence may be used beneficially to remove organic substances from the influent water.

Naturally occurring organic compounds in water supplies (sometimes referred to as aquatic humus) are relatively refractory materials, and their biological degradation is usually a relatively slow process. Thus in the application of microbiological processes to GAC, various workers have proposed to increase the biodegradability of these substances by applying an oxidation pretreatment process. Ozone has been the most favored oxidant for this purpose. The combined use of ozone and GAC for the removal of organic substances from water has been termed the biological activated carbon (BAC) process. Proponents of this process contend that BAC can extend the lifetime of GAC columns almost indefinitely, provided that microbiological colonies can be maintained. Treatment efficiencies during such extended lifetimes ordinarily do not equal those of fresh carbon, but the proponents of the BAC process contend that longer empty bed contact times in the carbon can be used to obtain desirable treatment efficiencies. According to this view, the increased capital costs associated with longer GAC contact times is more than offset by the avoidance of GAC reactivation or replacement costs.

Most of the data on which these conclusions have been based involve the application of ozone with activated carbon adsorption in European waterworks. Few cases have been studied in which the performance criteria match those required by U.S. drinking water regulations; that is to say, the operational criteria used in Europe to evaluate the BAC process do not correspond exactly to the minimization of THM's. For this reason, the U.S. Environmental Protection Agency (EPA) is sponsoring several pilot-scale investigations to evaluate GAC adsorption for the direct removal of THM's or THM precursors. This report describes the results of one such investigation. The study location is Shreveport, Louisiana -- the southern part of the United States. The test water is taken from Cross Lake, the principal water supply for the City of Shreveport. Cross Lake contains relatively high levels of THM precursors, but it is relatively uncontaminated by anthropogenic sources. A pilot study was carried out to evaluate GAC adsorption with and without preozonation as a means for removing these high levels of precursors. In addition, the study sought to examine other unit processes such as traditional alum flocculation and rapid mixed-media filtration for the removal of these substances. A variety of chemical and microbiological parameters were measured in the pilot plant and in associated laboratory experiments to obtain more information on the physical, chemical and biological processes that occur in GAC filters. Parallel to this effort, studies were taking place in the Thomas L. Amiss treatment plant of the city of Shreveport to assist municipal authorities in developing approaches to the minimization of trihalomethanes in the city water supply.

SECTION 2

CONCLUSIONS

The pilot-scale portion of this study has shown that GAC columns may be operated for extended lifetimes by an optimization of physical and microbiological processes that occur in these columns. Using THM formation potential (THMFP) as the principal analytical criterion, water from a southern U.S. reservoir has been treated effectively for a period of 1 year using a combination of alum flocculation, mixed-media filtration, and 24 minutes of contact with Filtrasorb-400 GAC. THMFP of the product water was less than 0.10 mg/L during this period, except on two occasions.

Engineering and cost analyses have been conducted for the addition of a 24-minute GAC contact period to an existing plant using the same reservoir as the water source. The analyses show that costs are not unreasonable: for 1-, 10-, and 100-MGD plants, additional costs of \$0.11, \$0.20 and \$0.13 /KG were computed.

The addition of ozone before GAC adsorption extends the lifetime of GAC columns, presumably by direct oxidative reduction of THMFP and by encouraging microbiological removal mechanisms in the GAC columns. Under the conditions used in this study, ozone-treated GAC columns produced product water with THMFP values of less than 0.10 mg/L for 67 weeks. Optimization of the dose and contact time of ozone may result in long enough service times to offset the additional costs of ozone production.

An analysis of the chemical and microbiological data from the pilot study suggests the following conclusions regarding the pilot plant operation:

- a. Traditional treatment consisting of alum flocculation, sedimentation, and mixed-media filtration results in the removal of 30% to 40% THMFP, with more efficient removal occurring in the summer periods. Except for occasional periods in the winter months, the product of this treatment has THMFP values well in excess of 0.10 mg/L.
- b. Oxidation with ozone is not an effective method per se for the removal of THMFP. For the relatively low doses (2-6 mg/L) used in this work, 5% to 20% destruction of THMFP was observed. Combined with traditional treatment, ozonation produced water that met the 0.10 mg/L THMFP criterion only 20% of the time.

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- c. The addition of GAC columns to traditional treatment with or without ozonation is an effective means for controlling THM precursor levels. Various data point to the following mechanisms as those responsible for the sustained removal of natural organics from the GAC columns:

- (1) Physical adsorption: this process is prevalent during the early stages of operation and shows the expected decline in rate as macropore sites become saturated and the process is limited by pore diffusion. But, as other workers have shown, the capacity of GAC for natural organics is very large if the micropore capacity is fully utilized.
- (2) Microbiological degradation: this process is temperature dependent and accounted for the removal of approximately 0.21 moles of carbon/M³ GAC-hr. (or approximately 0.13 mg THMFP/M³ GAC-hr.) during its optimum period.

- d. Preozonation before GAC adsorption, at least at the doses used in this study (generally 2-3.5 mg/L) does not have a dramatic effect on the removal of THM precursors. Over the eighty week period of the operation of the pilot plant, the unozonated GAC columns outperformed the ozonated columns in terms of cumulative TOC or THMFP removed. In terms of percentage removal, however, the two trains performed almost identically. A detailed analysis of the data obtained during the eighty week study period suggests that natural organics are slightly less adsorbable and slightly more biodegradable after ozonation, making the ozonated and non-ozonated GAC columns perform very nearly the same.
- e. Optimization of the ozone dose and reactivation regime should lead to enhanced microbiological removal, which would extend the lifetime of GAC for THMFP removal.

These two processes combine to yield a sustained period of THMFP removal. During the early stages, the removal is largely due to physical adsorption, but in the latter part of the study, microbiological processes appear to prevail. The intermediate period, referred to by some as a pseudo steady-state period, is apparently due to a combination of the two processes.

The use of total organic carbon (TOC) as a surrogate parameter for THMFP is not advised, at least on water systems such as Cross Lake, Louisiana. Though the surrogate is satisfactory most of the time, temporary inconsistencies occur with substantial frequency, making the overall correlation poor ($r^2 = 0.6 - 0.7$).

Parallel to the pilot study, the project team also assisted personnel of the T.L. Amiss plant of the city of Shreveport to analyze their treatment process to minimize THM levels. These studies are incomplete, but they suggest the following conclusions:

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- a) Instantaneous THM levels in the Amiss distribution system are extremely high by MCL standards, with an approximate range from 0.10 mg/L in the winter to 0.35 mg/L in the summer.
- b) A substantial fraction of these THM levels is produced on prechlorination, a common practice at the Amiss plant. During summer months, levels in excess of 0.10 mg/L often occur after a detention time of only 10 to 20 minutes beyond prechlorination.
- c) Elimination of prechlorination results in more effective coagulation of precursors in the sedimentation basins. The result is not only that lower THM levels leave the Amiss plant, but lower ultimate values are achieved in the distribution system.
- d) Control of pH levels after lime stabilization is an ineffective means for minimizing THM formation.
- e) Control of chlorination practice alone cannot solve the THM problem in systems such as the Amiss plant. Other measures that may be used are GAC adsorption, as indicated by the pilot study, and substitution of an alternative disinfectant for chlorine.
- f) If chloramination is to be used in place of chlorination, it must be substituted throughout the plant, at least during summer periods. The control of primary producers in the plant basins, taste and odor problems, and manganese levels in the product water then become management problems that will require renewed attention. Preoxidation with permanganate, ozone, or other oxidants will almost surely be required at certain times in southern U.S. plants.

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RECOMMENDATIONS

This project has shown that biologically enhanced removal of THM precursors is possible. Full-scale studies should be encouraged to optimize the process. Particular attention should be given to the development of regimes for partial reactivation of the GAC beds in some type of rotary fashion so that biological and physical adsorption may be coordinated and the entire process optimized.

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SECTION 4

BACKGROUND

FORMATION OF TRIHALOMETHANES IN DRINKING WATER TREATMENT

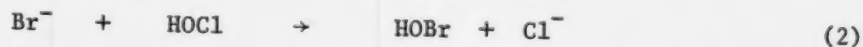
Chloroform, CHCl_3 , and three other trihalomethanes, CHCl_2Br , CHClBr_2 and CHBr_3 , were discovered in finished Rotterdam drinking water by Rook in the early 1970's (1), and almost simultaneously by Bellar, Lichtenberg and Kroner (2) in Cincinnati. Although there are still elements which are poorly understood, the following appear to describe our present knowledge concerning the formation and occurrence of THM's in drinking waters:

1. The trihalomethanes are generally not found in raw water sources but are found almost ubiquitously in finished water supplies where chlorination is used (3, 4).
2. The trihalomethanes are formed in the process of treatment by a reaction often symbolized as follows (5):



where CHX_3 is the general formula for THM's.

3. Bromine enters into the reaction by oxidation of naturally occurring bromide by hypochlorous acid (HOCl), the active chlorinating agent in water (6)



Hypobromous acid, HOBr , is formed in this process and competes for precursor molecules with HOCl .

4. "Precursor" is a general term expressing all possibly types of chemical species which may react with hypohalous acids to yield trihalomethanes (THM's). While the chemical identity of these precursors is unknown, and may never be known, they appear to be naturally occurring organic compounds rather than man-made (synthetic) compounds (1). Natural compounds or compound classes which have been shown to act as precursors include humic and fulvic acids from soils and aquatic sources (7), plant pigments (8), and algal extracellular products (9, 10).

5. The reaction symbolized by equation (1) is an incomplete description of the prevailing chemistry in at least two aspects:

a. THM's containing iodine (but not fluorine) may also be formed if iodide is present, and CHCl_2I has been observed in several cases (11).

b. Other halogenated organic compounds besides the THM's are also formed (10). The total amount of organic bound chlorine (TOX) formed will often exceed that found in the form of the THM's by a factor of 3-5 (12, 13).

c. The reaction forming THM's and TOX is accelerated by high pH and high temperature conditions suggesting a complex multistep reaction sequence (14).

The full significance of Rook's finding is still developing, primarily because world health authorities are concerned with the occurrence of halogenated organic compounds in man's diet (15). After its discovery in drinking water, chloroform was banned by the U.S.F.D.A. from drug and food products as a result of studies on test animals which were interpreted to show that chloroform was a carcinogenic agent (15). In 1979, the U.S.E.P.A. published regulations establishing a 0.10 mg/L limit on the sum of the four THM's, based again on toxicological considerations (16). While debate continues on the issue, the present consensus seems to be that THM's (and possibly the level of TOX) should be regulated at some level in finished drinking water. The value of 0.10 mg/L promulgated by the U.S.E.P.A. is purportedly a compromise, taking into account the possible carcinogenicity of the THM's as well as the obvious beneficial aspects of water chlorination (17). Toxicological and epidemiological research on this issue is still emerging (18).

CONTROL OF THM'S IN PUBLIC WATER SUPPLIES.

Several strategies have developed for the control of THM levels in finished drinking water including the following (19):

1. Minor modifications of the water treatment process such as to abate the use of chlorine or delay its application until precursor removal has been accomplished by traditional treatment practices.

2. Substitution of an alternative disinfectant for chlorine such as chloramines, chlorine dioxide or ozone.

3. Use of advanced treatment processes for removal of THM's in post-treatment.

4. Use of advanced treatment processes to remove the THM precursors before the application of chlorine.

Minor Process Modification for THM Control

Perhaps the simplest process modification proposed for THM control is to delay the point of chlorination until precursor removal has been effected, at least in part. Water utilities often add chlorine prior to flocculation/clarification basins or prior to rapid filters. In certain cases the elimination of prechlorination or mid-point chlorination will lower THM levels in the product water to acceptable values (5). THM production may also be minimized by lowering chlorine dose (20) and by lowering the pH of the product water (14). The latter is not a flexible treatment alternative, however, since pH is used to control corrosion in distribution systems.

Use of Alternatives to Chlorine in Water Treatment

Chlorine is used in drinking water treatment plants not only for disinfection of bacteria, but also as an agent for taste and odor control, an oxidant for control of iron and manganese, and to improve floc formation (21). Ozone and chlorine dioxide have been shown to possess similar properties and are used in Europe more extensively than in North America (22). Chloramination is not an alternative to chlorine as an oxidizing agent, but it has served as an alternative disinfectant in Dallas, Texas; Jefferson Parish, Louisiana; and Huron, South Dakota among other locations. Studies at these sites have shown THM levels to be lowered considerably when compared to chlorination (23). THM's are also not formed by ozonation or chlorine dioxide (24), but these are costly alternatives to chlorination (25).

Two studies on the use of chloramines in lieu of chlorine have been reported. At the Jefferson Parish, Louisiana works, chloramination is used exclusively for disinfection. THM levels range from 5-10 $\mu\text{g/L}$ in the finished water, well below the 0.10 mg/L limit (23). At Huron, S.D. a systematic study of the effect of substitution of chloramines for chlorine was carried out by Norman *et al.* (26). Total THM levels dropped from 200-250 to *ca.* 50 $\mu\text{g/L}$ at two distribution system sites as a result of chloramine substitution. No detrimental effect on microbiological quality was observed.

Removal of THM's by Post-Treatment

Two processes deserve serious consideration for removal of THM's once formed in water plants. They are:

- a. activated carbon adsorption
- b. aeration

Several works have examined the use of activated carbon in both powdered and granular (column) forms. For either case costs for removal of THM's are high by present standards (19). Aeration is a more viable alternative, at least for the more volatile THM's, and active aeration systems have been reviewed by Love *et al.* (19) and by Smith (27).

It should be noted that attempts to remove THM's by post-treatment suffer from an inherent aspect of THM production; viz. THM production continues in the distribution system as long as precursors and a residual level of hypohalous acid remains.

Advanced Treatment Options for Removal of Precursors

Because THM precursors are of no definite chemical type, treatment alternatives for their removal must be broadly applicable processes. As noted above, it is generally assumed now that fulvic and humic acids are precursors. These are thought to be polymeric, anionic organics with both aliphatic and aromatic constituents (28). Algal metabolites and plant pigments may have quite different structures and physical properties (8-10). Therefore, a single process may not be successful for removal of all of these substances with equal efficiency. Nonetheless, at least four processes suggest themselves as alternatives for precursor removal:

a. oxidation with strong oxidants such as ozone (23, 29), chlorine dioxide (30), potassium permanganate (31), and catalytic oxidation processes such as ozone or hydrogen peroxide with UV radiation (29). With the exception of the catalytic oxidation processes, these oxidation procedures have not been successful for destruction of THM precursors. Costs are high, destruction rates are low, and in one case (ozone) precursors apparently are formed by chemical oxidation, as well as destroyed (32).

b. reverse osmosis. This and other membrane processes are theoretically capable of removing precursors in high yield. Laboratory water purification units often use RO modules for this purpose with good success. However, the costs are exorbitant by municipal treatment standards and no use of RO systems for this purpose is known at this time.

c. adsorption with resins. A substantial fraction of the organic material in surface water sources may be removed by filtration through anion exchange or neutral resins (33). Anion exchange resins are generally superior to neutral resins but regeneration may be incomplete in either case.

d. adsorption with activated carbon. Both powdered and granular activated carbon have been used for THM precursor removal. Both are capable of removing a substantial fraction of the organic carbon from natural waters, although granular carbon is generally preferred since it may be recovered and recycled after reactivation. A more detailed discussion of this topic is given in the following section.

REMOVAL OF THM PRECURSORS BY ACTIVATED CARBON ADSORPTION

A very large body of knowledge has accumulated on the properties of activated carbons and their use in water purification. It is beyond the scope or purpose of this report to review all of this information. Several reference works are available (34, 35, 36) in addition to published proceedings of conferences on activated carbon adsorption (37, 38, 39).

One fact emerges very clearly from this compendium, i.e. the details of the mechanism of the absorption of organic compounds by granular activated carbon columns are still not well understood. This is particularly true for complex mixtures which are typical of environmental samples. It is not possible to predict a priori the adsorption behavior of mixtures, even on a batch basis. And it is not yet possible to accurately scale up batch data for the design of pilot or full scale adsorption systems with complex, changing feed stocks.

Of particular interest to this research project is the current controversy over the interpretation of long-term GAC column performance data. Figure 1 is a typical plot of a group organic parameter (total organic carbon) for extended operation of a GAC adsorber using settled water at the influent. Plots such as this have been reported by several groups including Symons and coworkers (40), Wood and Demarco (41), and by Cairo et al. (42). All have the same general form and show less than complete exhaustion of the GAC filters after being in service for several months. The data from these studies often show a region of pseudo steady-state removal such as that shown in Figure 1. It is the interpretation of this pseudo steady-state region around which the current controversy revolves.

The European Experience

Rice and coworkers have summarized European water treatment practices in two reports prepared for the U.S. Environmental Protection Agency (43, 44). In these reports a new treatment technique not practiced in the United States was reported, i.e. aerobic biological oxidation on filter media (sand, anthracite and granular activated carbon). In the case of GAC filters, operational lifetimes were said to be extended well beyond the period of pure adsorption by a biological mechanism in which biodegradable organics were metabolized by bacteria growing in the filters. Refractory organics could purportedly be removed by the addition of an oxidation step prior to the GAC filters. Combinations of ozone (for oxidation) and GAC (for adsorption and long term biological removal) were said to be operating effectively in several European plants including Rouen la Chapelle, France; in the Dohne plant at Mülheim, Federal Republic of Germany; and at the Lengg plant at Zurich, Switzerland. Rice and coworkers concluded from a study of the European literature that pre-ozonation followed by activated carbon adsorption results in:

- Increased capacity of the carbon to remove organics (by a factor of about 10).
- Increased operating life of the carbon columns before having to be reactivated (up to 3 years), especially if the GAC can be kept free of halogenated organics.
- Biological oxidation of ammonia in inert media and GAC columns, which occurs simultaneously with removal of dissolved organics.
- Use of less ozone or less GAC for removing a given amount of organics

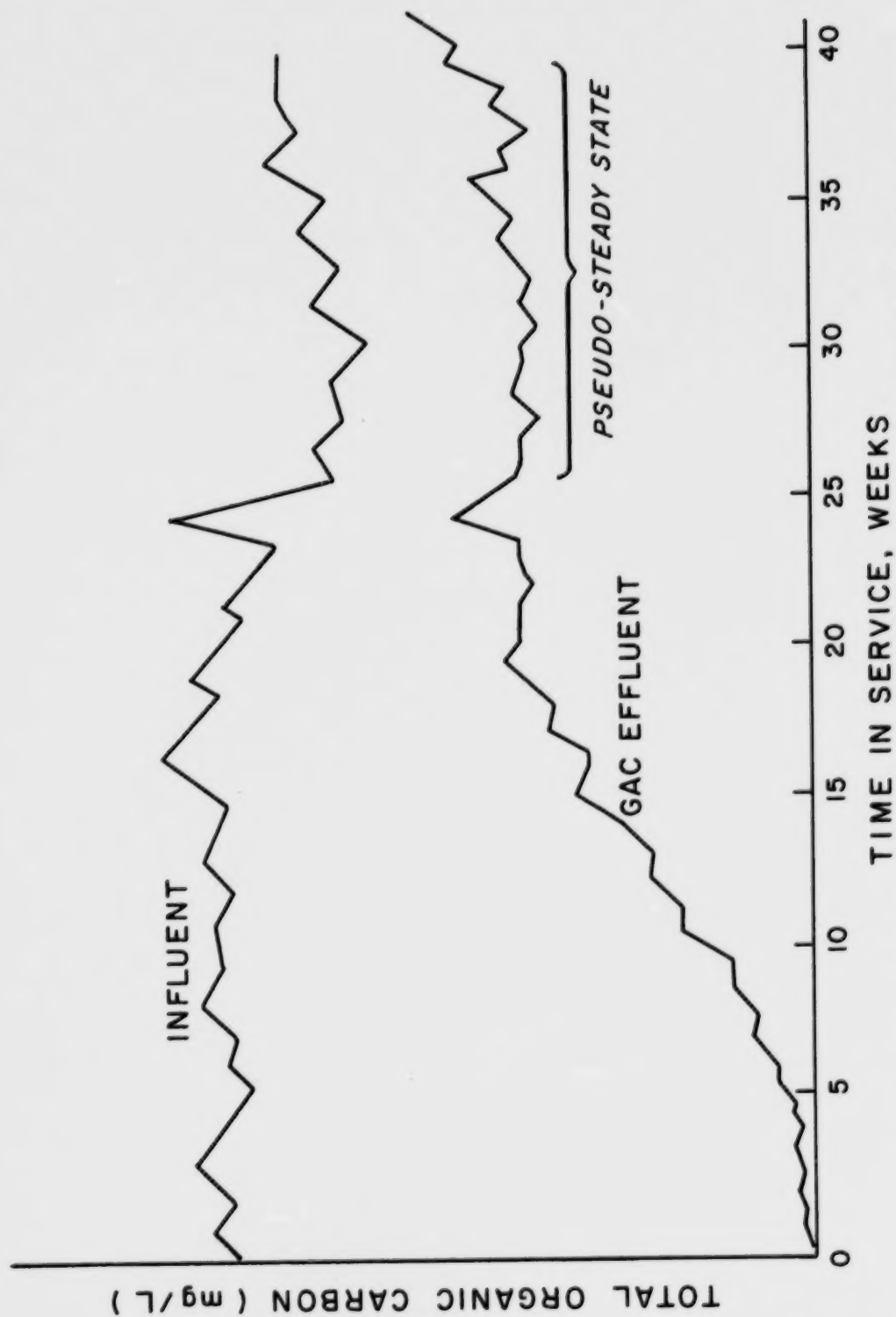


Figure 1. Typical Performance Curves for GAC Adsorbers in a Drinking Water Treatment Application.

than using either process alone. (44)

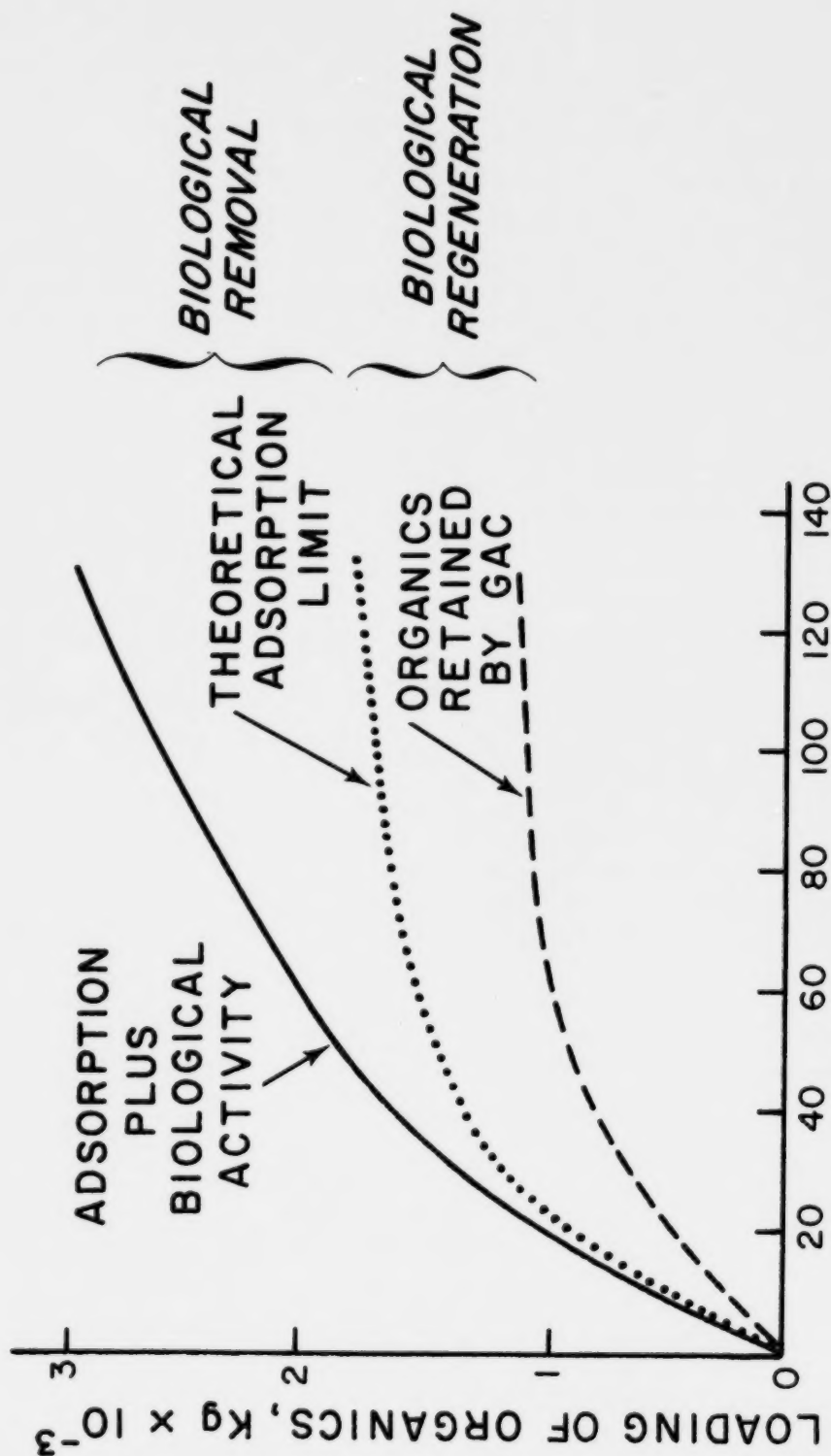
On the basis of these conclusions Rice and Miller coined the term Biological Activated Carbon (BAC) to denote a "combination of treatment processes consisting of (1) ozonation followed by (2) filtration through an inert medium, such as sand or anthracite, followed by (3) adsorption in GAC columns or beds" (45).

The majority of the substantive data used by Rice and coworkers has been developed by the group of Professor Heinrich Sontheimer and coworkers at the Engler-Bunte Institute of the University of Karlsruhe. Figure 2 shows the results of a study in collaboration with Poggenburg and others at the Düsseldorf treatment plant (46). According to Rice *et al.* (47) this study showed that the long-term capacity of GAC to remove organics exceeded the "theoretical" capacity of GAC by the difference between the solid and dotted lines in Figure 2. If one assumes that initial removal is due entirely to adsorption and limiting removal is due to biological removal, the rate of the latter may be calculated from the limiting slope as 500 gC/hr. Since the charge of GAC was 16,800 Kg, the biological rate is calculated to be 0.030 gC/Kg GAC-hr. In addition, this and other studies (45) purportedly showed that "biological regeneration" of GAC took place in the Düsseldorf columns, that is, microbes actually freed up GAC surface by metabolizing the organics which previously were adsorbed on this surface. The difference between the dotted and dashed lines in Figure 2 purportedly is a measure of biological regeneration.

Biological oxidation of organics in water supplies was recognized early on by Eberhardt (48, 49) at Bremen. In a review of his experience with biologically enhanced GAC processes, Eberhardt indicates that the degradation efficiency achieved is in the range of 1-4 g carbon per M³ of GAC per hour (49). At an effective density of GAC of 400 Kg/M³, this would correspond to a rate of 0.0025-0.01 gC/Kg GAC-hr. Thus, the value obtained in the Düsseldorf studies appears to be higher than that predicted by Eberhardt, but both groups would contend that a biological mechanism is responsible for sustained removals in GAC columns.

Poggenburg *et al.* (46) also measured the organics retained on GAC using an extraction procedure. The results shown in Figure 2 were compared with the theoretical adsorption limit calculated from laboratory scale batch absorption studies. The workers concluded that an apparent loss of organics occurred on the columns, measured by the calculated adsorption limit minus the organics recovered by extraction. On this basis they presumed "biological reactivation" of GAC was occurring. This conclusion is subject to criticism in view of the fact that the extraction efficiency cannot be 100% and at this time biological reactivation is not a confirmed process of importance. That is to say, it has not been conclusively shown that bacteria in GAC columns can metabolize adsorbed substrate.

Another very important study was conducted in the "Mont Valérien" plant by Mallevalle and others (50). Full scale tests were carried out to test the "biological activated carbon" concept. The test water was drawn from the river Seine and subjected to several processes including



WATER THROUGHPUT, m^3/Kg of GAC

Figure 2. Cumulative Loading of Organics on GAC Filters at the Düsseldorf Treatment Plant: Poggenburg *et al.* (46) after Rice *et al.* (44)

ozonation, rapid and slow GAC and sand filtration. Most significant were the findings that preozonation had little effect on removal rates in either sand or GAC filters, and that biodegradation rates were not appreciably faster on GAC than on sand.

The interpretation of the Mont Valérien data was made by Mallevalle in conjunction with Professor Andrew Benedek of McMaster University, Canada. Dr. Benedek, whose works include studies in both GAC adsorption (51) and biodegradation (52, 53) has become the spokesman for a view which de-emphasizes the rôle of biological degradation as the dominant mechanism to account for long term removal capacities, at least in drinking water treatment. This view is discussed in more detail in the following section.

Slow Micropore Diffusion in GAC Filters: An Alternative Explanation for Long Term Removal Capacities

Benedek summarized the interaction of adsorption and biological degradation on GAC filters in a paper presented at the ACS Meeting in Miami, Florida in 1979 (54). In this and subsequent papers Benedek and Mallevalle (50) have expounded on several aspects of the "BAC process" including the differences between its application for wastewater and potable water treatment. While conceding that microbiological colonies exist in GAC filters in both cases, Benedek and Mallevalle apparently depreciate the role that these species have in the removal of organic substances when a surface or groundwater source is the feedwater. Among the important conclusions of Benedek and Mallevalle are the following (54, 50):

1. Bacteria levels in GAC filters reach a steady state soon after being placed on line, with the microbial population being proportional to the cell concentration in the feed and the type and level of degradable organics in the feed.
2. Filtration of bacteria can account for a substantial portion of the populations found in GAC filters. For example, a cell density of one cell per 100 mL in a 2 GPM feed to a GAC filter will yield a population of approximately 10^6 cells over the period of a week.
3. Macromolecular synthesis leading to cell multiplication may also occur in GAC columns but the rate of this process is slower in potable water than in wastewater treatment due to the presence of more biodegradable organics in wastewater feedstocks.
4. Respiration leading to carbon dioxide production in GAC columns may be due in part to endogenous respiration of cells, i.e. respiration using internal sources of carbon rather than carbon removed from the feedwater.
5. The effect of ozonation on the removal of organics in GAC columns due to higher biodegradability is at least partially offset by lower adsorbability of the oxidized organics.

6. The long term removal of organics in GAC columns during potable water treatment is due mainly to adsorption rather than microbiological processes.

As an alternative to the microbiological removal mechanism, Peel and Benedek have refined models for adsorption of organics from water, recognizing a more important contribution of adsorption in *micropores* of the GAC (55-57). Below is a brief summary of the model.

Granular activated carbon adsorption is generally thought to occur by several steps (34):

1. Transport of the solute from the bulk of the solution to near the GAC surface.
2. Diffusion of the solute through a surface film to the exterior of the adsorbent ("film diffusion").
3. Diffusion of the solute into the pores of the adsorbent ("pore diffusion").
4. Adsorption of the solute onto the adsorbent.

On the basis of careful equilibrium and kinetic studies Benedek and coworkers were led to develop a dual parameter, or branched pore diffusion model for adsorption (55-57). This model more accurately takes into account slow pore diffusion processes which occur in the so-called micropore regions of the GAC. The net effect of including such terms is to provide for a larger effective surface for solute adsorption, which is manifested slowly after the "macropore" adsorption is exhausted. Thus, Mallevalle *et al.* (50) interpret the so-called "pseudo steady-state" region shown in Figure 1 as a region dominated by slow micropore diffusion rather than microbiological degradation processes. Cumulative removal plots such as Figure 2 are predicted entirely on the basis of the branched pore diffusion model without resorting to any postulate of microbial removal of solute (50).

It should be noted at this point that other workers have developed a similar approach to GAC column modeling. Recently Lee and Snoeyink (58) have utilized a model originally developed by Crittenden and Weber (59) to rationalize the adsorption behavior of commercial humic and fulvic acid extracted from peat. These authors point out the importance of careful, long term kinetics studies to evaluate the diffusional parameters for large molecules such as natural organics. The use of kinetic parameters obtained in this manner results in models for column performance which are in agreement in principle with the model of Benedek. Figure 3 shows the predicted breakthrough curves for humic acid adsorbed on WV-G carbon with various empty bed contact times (EBCT). It is apparent from Figure 3 that the longer the EBCT the better the performance of the filters. Or conversely, in columns of moderate EBCT (e.g. 15 minutes) adsorption will appear to "tail off" gradually and may even appear to reach a pseudo steady-state. With a variable influent concentration then it may

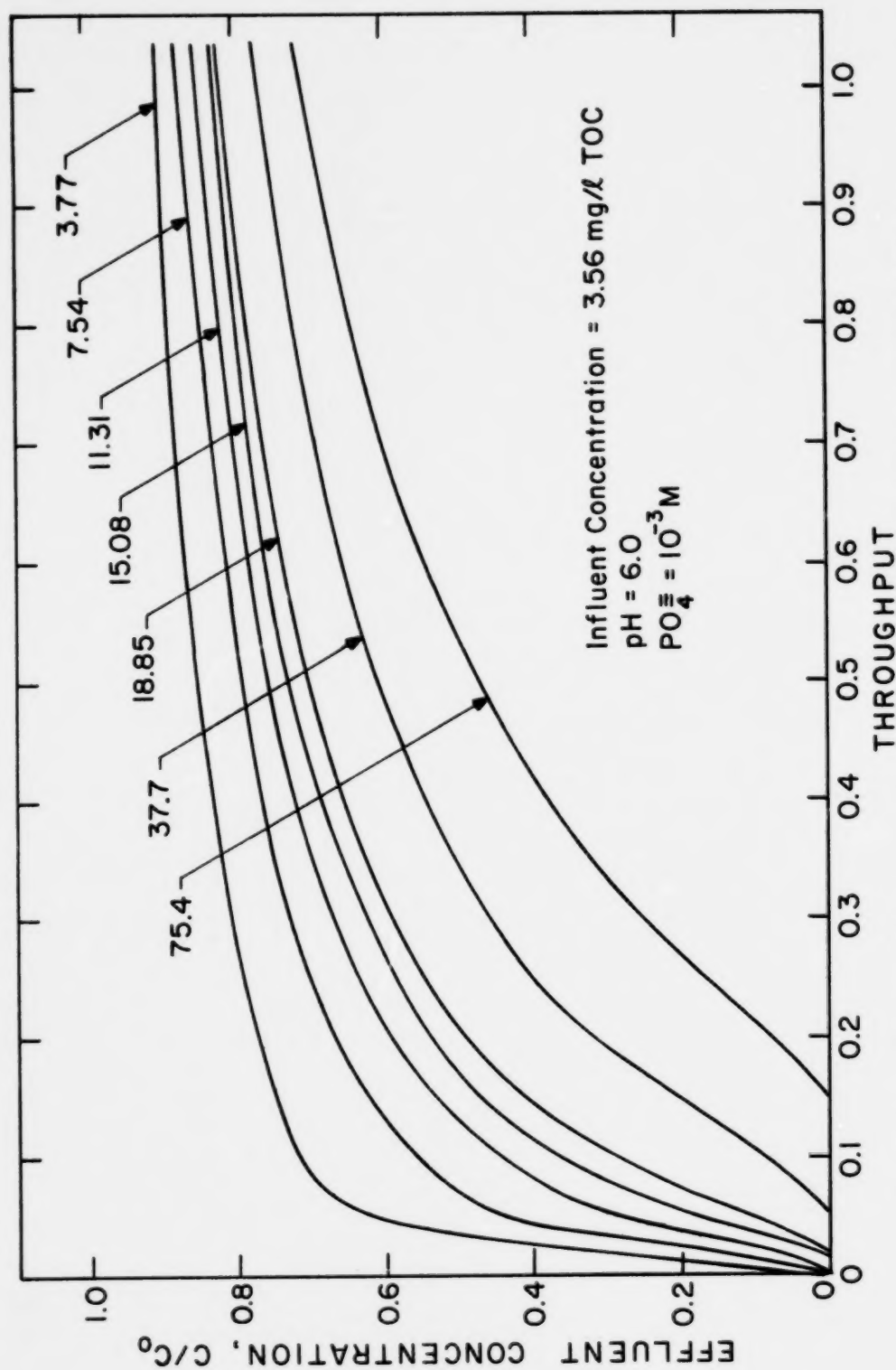


Figure 3. Predicted Breakthrough Curves of Peat Fulvic Acid Adsorbed by WV-G Carbon with Various Empty Bed Contact Times: Lee and Snoeyink (58).

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be extremely difficult to determine from GAC column performance data if a microbial steady state or micropore diffusion process is prevalent, or if both contribute to the removal process.

PURPOSES OF THE PRESENT STUDY

It is apparent from the foregoing discussion there remains some uncertainty in the role of microbiological vs. adsorption processes in GAC columns used for potable water treatment. The major purpose of this project was to add to the available base of data on this subject, while also providing other information on the control of THM's. The site chosen for the present study was one in which THM precursor levels were high and other anthropogenic organics were relatively low. The major portion of the project consisted in the design, construction and operation of a 10 GPM pilot plant to test the following unit processes for THM precursor removal:

1. Combined alum flocculation, settling and rapid mixed-media (sand, garnet and anthracite) filtration.
2. Ozonation, with long and short contact times.
3. Granular activated carbon adsorption, with and without preozonation.

In addition to accomplishing the principal objective, the project also attempted to determine the role of microbiological vs. adsorption processes in the GAC columns and to evaluate costs for the application of post-GAC adsorbers in a drinking water plant with high THM precursor levels. Finally, this project sought to develop a detailed data base on THM production in an actual treatment plant in the southern United States and to ascertain the most feasible methods for THM control.

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SECTION 5

PILOT SCALE EVALUATION OF THM PRECURSOR REMOVAL METHODS AND PROCEDURES

DESCRIPTION OF THE PILOT TEST FACILITY

The pilot plant is fully contained in a forty foot drop-frame Fruehauf trailer. Figures 4 to 6 are photographs of the exterior and interior parts of the trailer as it was initially equipped. The pilot plant was operated in two consecutive sub-phases Phase I-E-1 and I-E-2 lasting for 63 and 17 weeks respectively. In both sub-phases raw water from Cross Lake, Louisiana was treated in a Neptune-Microfloc Waterboy unit by alum flocculation, sedimentation and fast mixed-media filtration. Settled-filtered water from the Waterboy was the test medium for several subsequent water treatment unit processes including ozonation, GAC adsorption and sand filtration.

On entering the pilot plant, raw water first flows through either of two electrically operated two-inch valves. One valve is used to divert water to the waste line, and the other leads to a set of coarse filters in parallel. The valves are wired so that all of the water goes in one or the other direction and they are controlled by the Waterboy unit. From the coarse filters, the water can be fed directly to the Waterboy unit or first sent through a storage basin for holding if some type of chemical pretreatment (ozone, chlorine dioxide, etc.) is used. In both Phases I-E-1 and I-E-2 no preoxidant was used, however.

The Waterboy unit is a fully automatic water purification system which produces 10 GPM of low turbidity water. It consists of three chambers for flocculation, tube settling, and mixed-media filtration. At 10 GPM, the residence time for each chamber is 8.3, 15.6, and 5.5 minutes respectively. Incoming raw water is regulated by a float-operated valve which maintains a constant water level in the unit. Treatment chemicals are added immediately after the valve from 30 gallon tanks with small metering pumps. Chemically treated raw water enters the flocculation chamber from the bottom, is stirred at 12 rpm, and then flows into the settling tube chamber. As the water flows through the settling tubes, the suspended floc is retained and the settled water goes to the mixed-media filter chamber. From the top the (2.3 sq. ft.) filter is composed of 10" MS-4 coal, 10" MS-6 sand, 2" MS-7 Garnet, 1-1/2" MS-11 Garnet, 1-1/2" MS-13 Garnet, 2" MS-1-3/8" x 3/16" Gravel, and 3" MS-1-3/4" x 3/8" Gravel.

BEGIN
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FOR TABLE
AND ILLUSTRATIONS



Figure 4. External View of Trailer Containing Pilot Water Treatment Plant.

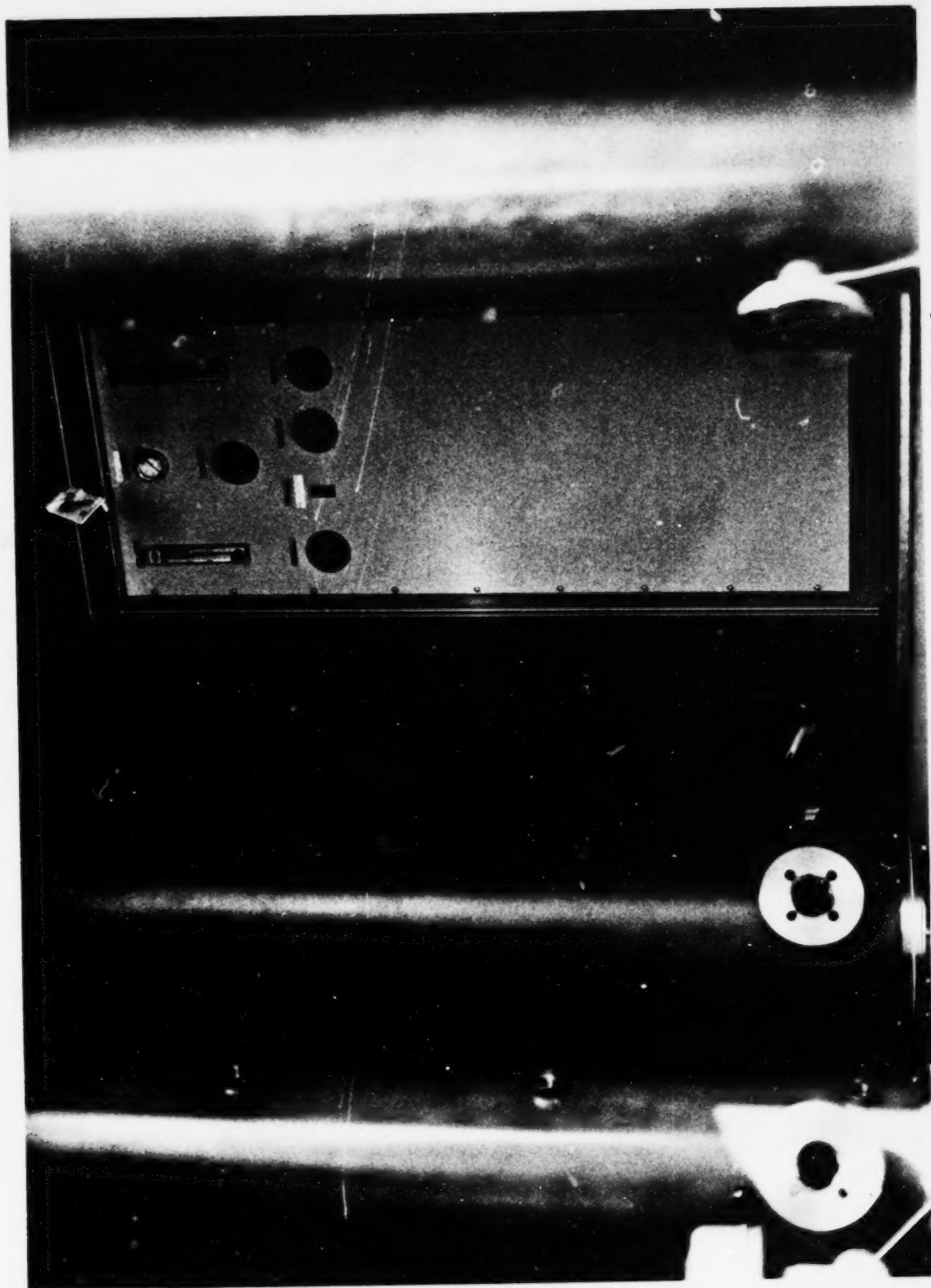


Figure 5. View of Ozone Generator (Center) and Two Unconnected GAC Columns (6' x 12" I.D. 304 SS).

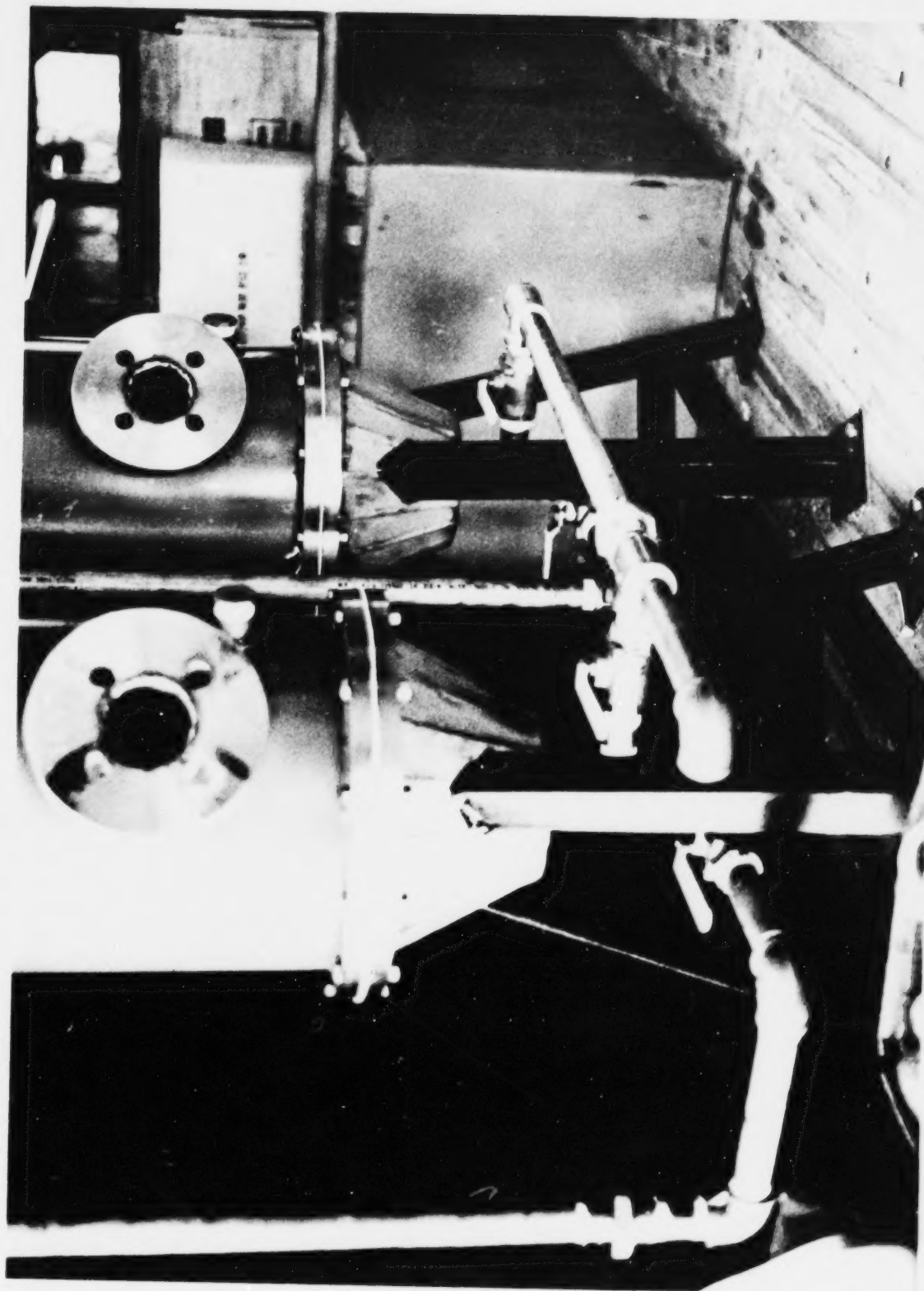


Figure 6. View of Lower Section of GAC Columns Showing Effluent and Backwash Lines.

The suction type filter is operated by a 1/2 hp centrifugal pump with the flow rate regulated by a 10 GPM Griswold flow controller. The filtered water from the Waterboy unit flows to a 600 gallon aluminum basin which serves as the reservoir for water to be used in the rest of the plant and which also is periodically used in backwashing the Waterboy filter.

When an 8 ft. (of water) filter headloss is detected, an automatic sequence of operations is performed by the Waterboy which cleans the filter and the settling tubes. A backwash cycle includes 8 minutes of filter backwashing at 40 GPM during which the wash water passes through the tube settlers and is siphoned from the settling tube chamber. The unit resumes normal operation with only 15 minutes of downtime.

Phase I-E-1 Flow Pattern

Figure 7 shows a schematic diagram of the flow pattern in the pilot plant during the first sixty-three week test phase (Phase I-E-1) extending from late December, 1979 to March of 1981.

From the backwash basin, 2 GPM of settled-filtered water are sent by a positive displacement pump through a pair of 12" ID 304 stainless steel columns 8 feet in height containing 4 feet (37 Kg) of Calgon Filtrasorb - 400 activated carbon. The columns (numbered 5 & 6) have ports for sample taking 4-1/2", 2'-1/2", and 3'-9-1/2", from the bottom. There is also a 3" flanged opening near the bottom for loading and unloading the carbon. An air release valve and pressure gauge are installed at the top of each column. All carbon columns in the pilot plant are similarly constructed.

Each set of carbon columns has its own backwash system consisting of a 150 gallon aluminum storage basin, a 1/2 hp centrifugal feed pump, and the necessary plumbing for backwash feed and effluent removal. A quick-release hose fitting is installed at the base of each column so that air sparging can be used during column backwash. Glass sight tubes are included as part of the backwash effluent system so that loss of carbon can be minimized.

Two sets of carbon columns receive water which has been ozonated. Six gallons/min. of settled-filtered water from the backwash basin is pumped into a cylindrical 304SS ozone contact basin operated at 5 psi. The ozone is introduced with a high speed turbine injector designed by Kerag (Switzerland) and manufactured by Howe-Baker (Tyler, Texas). The ozone is generated by a Howe-Baker "Escozone E4" ozone generator using oxygen from a liquid oxygen cylinder, stored outside the trailer. At 6 GPM, retention time in the ozone contact basin is 3.3 min. Immediately after the contact basin, 2 GPM of ozonated water is pumped to carbon columns 1 and 2. The remaining 4 GPM of ozonated water is released into a covered 304 SS ozone detention basin which is at atmospheric pressure. The ozone detention basin has two chambers in which the water level is determined by replaceable overflow pipes. In this study, only the maximum water level of 36" was used. This gives a detention volume of 15.6 gallons for the first chamber and 134 gallons for the second chamber for a combined

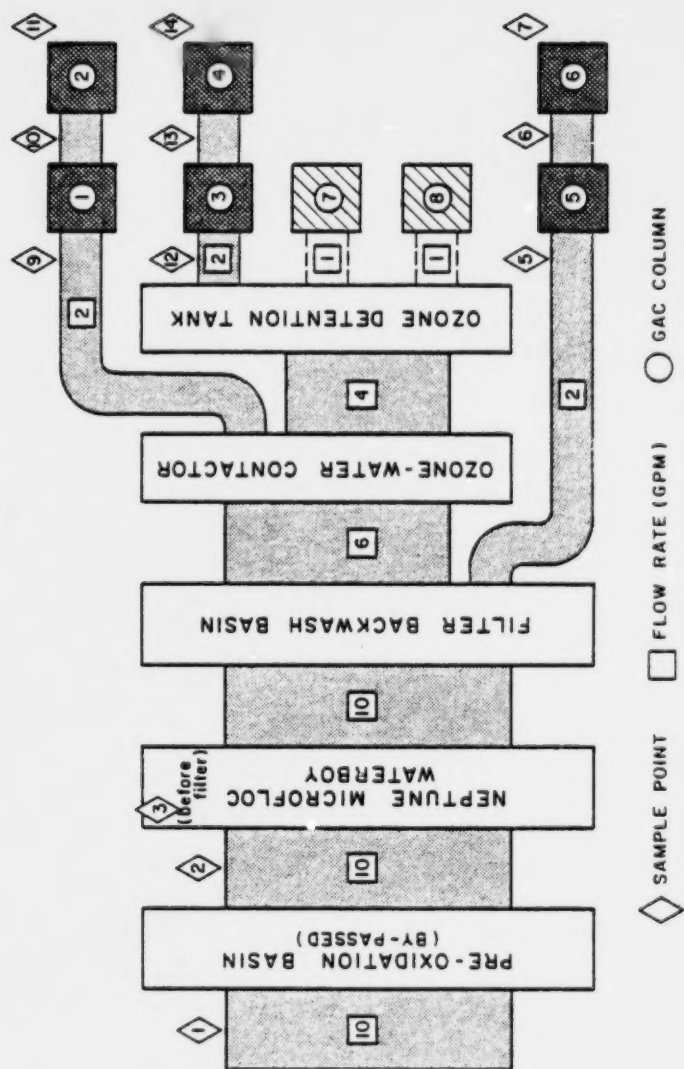


Figure 7. Schematic Flow Diagram for Shreveport Pilot Treatment Facility in Phase I-E-1.

volume of 150 gallons and combined detention time of 37.5 minutes at 4 GPM. After this detention time, 2 GPM are pumped to carbon columns 3 and 4. The remaining 2 GPM of water overflows to the waste line.

Solenoid operated valves are used for composite sampling at 18 points in the treatment process. A switch panel is used to operate the valves individually or they can be timer controlled. The samples are transferred with 1/8" I.D. black teflon tubing to glass bottles in two small refrigerators. Figure 8 shows the flow diagram and sampling points for columns receiving ozonated water. Sampling will be discussed in more detail in later sections of this report.

GAC columns 7 and 8 shown in Figure 7 were not monitored routinely, since they were used in the first operational phase merely to obtain samples of biologically active GAC for laboratory studies.

Phase I-E-2 Flow Pattern

During March 1981, some operational changes were made in the pilot plant. Carbon columns 1 and 2 were dismantled and this line was no longer included in the treatment scheme. Four new columns were set up in parallel to receive 2 GPM water through each column. Two received ozonated water, while the other two received water from the backwash basin. In each pair, one column contained 4 ft. of fresh activated carbon (F400) and the other had 3-1/2 ft. of filter sand, 2" MS-13 Garnet, 2" MS-1-3/8" x 3/16" Gravel, and 2" MS-1-3/4" x 3/8" Gravel. In each set, the effluent line from the sand filter was connected directly to the waste line. The effluent line from the carbon filter remained connected to the column backwash basin and this water was used to backwash both columns in the set.

The feed lines for both sets of columns are plumbed the same. Water is centrifugally pumped to the columns with the rate to each column controlled by a 2 GPM Griswold flow controller. Columns 9 (sand) and 11 (carbon) receive ozonated water and columns 10 (sand) and 12 (carbon) receive non-ozonated water. Columns 3, 4, 5 and 6 were operated unchanged (figure 9).

The capacity of the Waterboy unit was increased to over 12 GPM by substitution of a ball valve for the flow controller in the effluent line. Since the rate of water going through the ozone detention basin was increased to 6 GPM, the detention time decreased to 25 minutes.

SUMMARY OF PILOT PLANT OPERATION

The pilot plant began continuous full operation on December 29, 1979 after several weeks of testing and delay caused by failure of the ozone turbine diffuser. When the Waterboy unit was first operated in September 1979, it produced 10 GPM of low turbidity water, but within a few months, the output had been reduced by biological fouling of the raw water line. At times, the reduced water supply caused intermittent operation of the effluent pump which resulted in more turbid water (min. 0.5 NTU). A

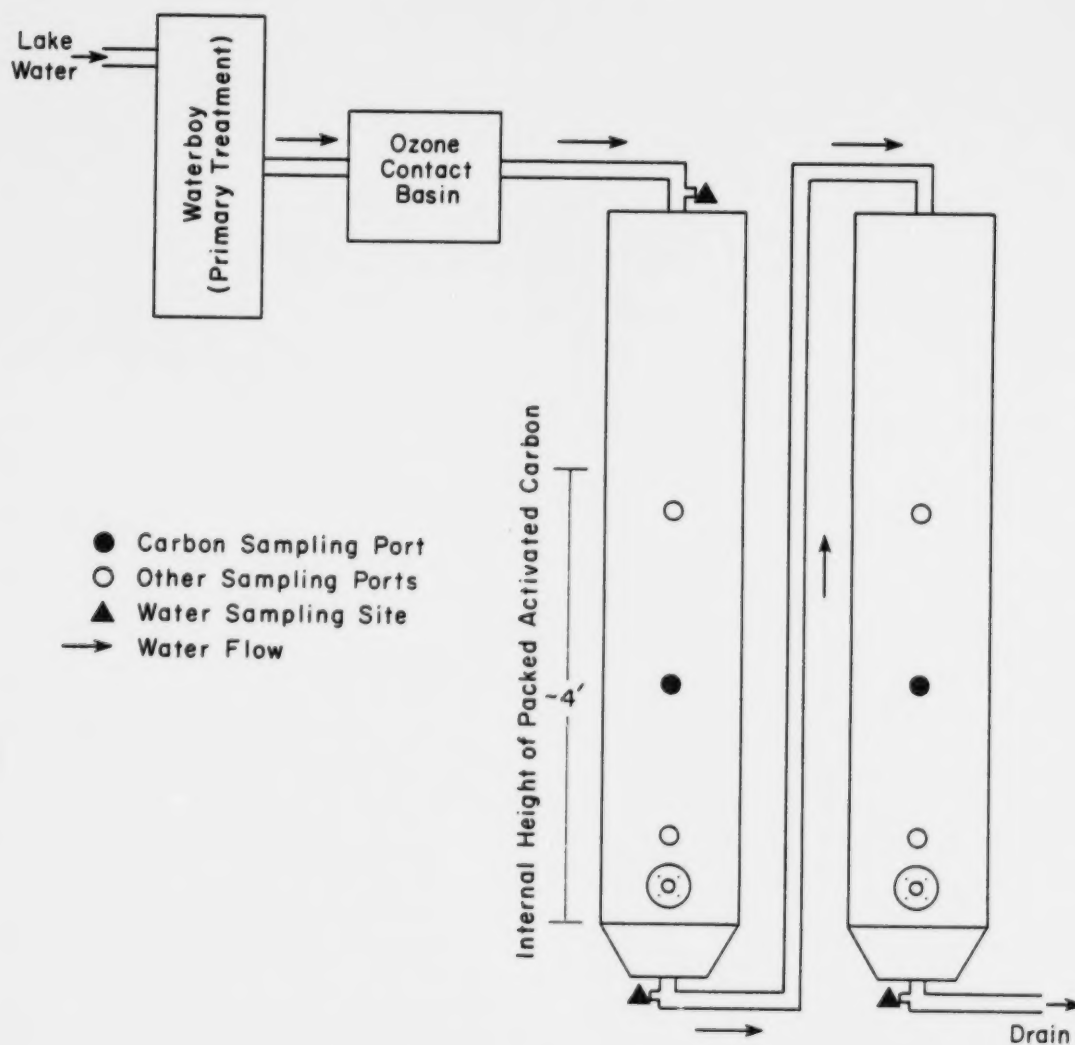


Figure 8. Flow Diagram Showing Water and GAC Sampling Points for Columns Receiving Ozonated Water. Sample Points are Identical for Columns Receiving Unozonated Water.

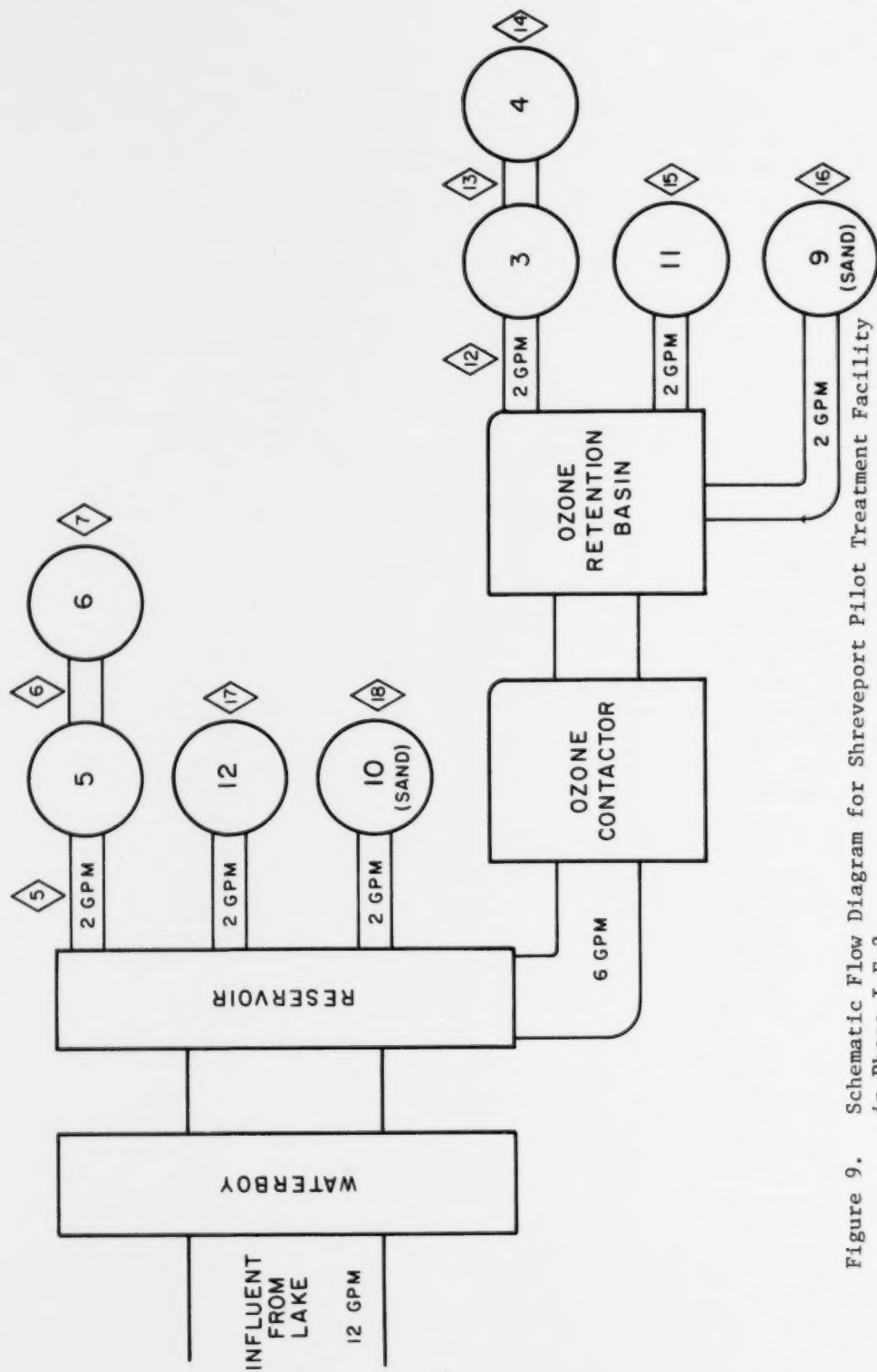


Figure 9. Schematic Flow Diagram for Shreveport Pilot Treatment Facility in Phase I-E-2.

procedure for cleaning the raw water line with a small rubber ball "pig" was developed and in October 1980 an adequate water supply was established. In warm periods the line was cleaned every six to eight weeks.

In the summer of 1980, the raw water supply was interrupted on several occasions by air binding of the raw water pump. The problem became so severe that the pump was moved closer to the lake's surface in order to reduce the suction lift. This ended all problems with the raw water supply in the first part of the study.

When columns 9, 10, 11 and 12 were brought on line in March 1981, the Waterboy unit's output was increased to >12 GPM (12 GPM needed by the columns plus refilling of the filter backwash basin). Although the Waterboy unit was designed for 10 GPM operation, after replacement of the 10 GPM Griswold flow controller with a ball valve, >12 GPM of finished water was obtainable. Due to the increased flow rate causing less efficient operation of the tube settlers, the unit required more frequent backwashing. The backwash sequence was modified so that less filter backwash water was used during each backwash. Also the filter media was manually agitated more often so that longer filter runs could be accomplished. The alum feed rate was reduced from 50 to 35 ppm to reduce floc carryover to the filters. With an increased frequency of cleaning of the water line, the raw water supply was just sufficient to provide the necessary water.

In January 1980, a gradual decrease in the alkalinity of the raw water prevented good flocculation in the Waterboy unit. Beginning February 8, a solution of NaOH was added to the raw water before the alum in order to raise the alkalinity. Sodium hydroxide was chosen over lime Ca(OH)_2 , which is used in the Amiss plant, because it would not interfere with carbon dioxide measurements later in the treatment process. The feed rate of NaOH was determined by the pH of the raw and finished water. The pH of the finished water was kept approximately 1 pH unit below the pH of the raw water. This greatly improved floc formation and lowered the turbidity of the finished water to less than 0.5 NTU. Addition of NaOH was continued until August, but at a significantly reduced rate after the winter months. Sodium hydroxide was also added from December 23, 1980 to May 15, 1981.

When the Waterboy unit was first operated, the alum feed rate was varied according to the turbidity of the finished water in order to minimize the amount of alum used. Due to the wide fluctuations of turbidity of the shallow lake and unsupervised operation of the pilot plant, a slightly higher feed rate of alum than is normally needed was finally chosen. Since the pH adjustment was used in periods of low natural alkalinity of the raw water, fifty ppm of alum was found to work well year round and was initiated on March 8, 1980. This dosage was continued until March 3, 1981 when it was reduced to 35 ppm.

In the first 2 weeks of full operation, the ozone generator was found to have a defective flowmeter which was replaced. Until it was replaced on January 12, 1981, approximately 45 cu. ft./hr. of oxygen was

TABLE 1. SUMMARY OF PILOT PLANT OPERATION

PHASE I-E-1 (Figure 7)

December 29, 1979 - March 13, 1981

PHASE I-E-2 (Figure 9)

March 17, 1981 - July 23, 1981

MAJOR OPERATIONAL ABNORMALITIES

		<u>Situation</u>	<u>Reason</u>
1980	Feb. 19 - Feb. 22	No ozone fed	Ozone generator down
	June 10	Plant off	Raw water pump
	June 15 - 20	Plant operated inter- mittently	Raw water pump
	June 29 - June 31	Plant off	Raw water pump
	July 10 - 14	Plant off	Diffuser feed pump
	Oct. 15 - 17	Column 1 & 2 off	Feed pump
	Oct. 21	Plant off	Raw water pump
	Nov. 1 - 3	Plant off	Cleaned raw water line
1981	Feb. 6	Plant off	Raw water pump
	Feb. 11 - 13	Plant off	Frozen raw water line
	March 13 - 20	Plant off	Major changes in operation
	April 13	Plant off	Raw water pump was moved
	April 27	Plant off	Raw water pump
	Apr. 29 - May 5	Ozone diffuser not operating	Bearing noises
	May 6 - May 13	No ozone added	Diffuser and generator were being repaired
	June 6	Plant off	Raw water pump submerged

used to generate ozone instead of the required 18 cu. ft./hr. On February 19, an oxygen leak developed in the ozone generator which severely limited the amount of ozone delivered to the diffuser. This was repaired by Howe-Baker personnel on February 22. At this time it was decided that the amount of oxygen used in ozone generation be cut from 18 cu. ft./hr. to 9 cu. ft./hr. as an economy measure. The ozone generating voltage was increased so that the same ozone feed rate was maintained. According to the manufacturers, at least 18 cu. ft./hr. of feed gas is required by the ozone diffuser for proper operation, so 9 cu.ft./hr. of atmospheric air was admitted to the suction line of the injector. After several months of operation, restricting the amount of air admitted became difficult due to air leakage around the shaft of the diffuser. This problem was corrected when the injector shaft's bearings were replaced in May, 1981.

The ozone generator developed several problems during the operational period. One problem is that the O-rings which seal the glass cooling tubes shrink with use. This causes leakage of ozone and allows the tubes to become unsealed which requires full disassembly to repair. This has occurred on four occasions. Also, every one of the five ozone generator rods were not operational at all times due to blown fuses and bad contacts. There was also some leakage of oxygen inside the generator, all of which required increases in the voltage of the unit to maintain a constant ozone concentration. On February 20, 1981, these problems were corrected and the voltage was decreased.

Applied ozone dose rates were as follows: from start-up to February 1, 1980, 6.3 mg/L; from February 2, 1980 to June 10, 1980, 2.0 mg/L; from June 11, 1980 to May 12, 1981, 2.5 mg/L and from May 13, 1981 to July 23, 1981, 3.4 mg/L.

The flow rates of all columns in the first part of the operational period were set with variable speed positive displacement pumps. The actual flow rates were first found using turbine-type flow meters but after several months of operation the flow meters began to give erratic results and required excessive cleaning. After mid-summer, the flow rates were found by manual measurement of the column effluent entering the column backwash basins. The flow rates were reset after each measurement. They usually remained constant over a week's operation with only about a 5% drop and were found to be less erratic than first indicated when the flow meters were used for measurement.

The Griswold flow controllers on columns 9, 10, 11 and 12 operated exceptionally well as long as the pressures of the columns remained within the specifications of the controller.

ANALYTICAL CHEMISTRY: METHODS AND PROCEDURES

Composite Sampling

As noted above solenoid operated valves are used for composite sampling. These are located at the sample points denoted in Figure 7 for Phase I-E-1 and Figure 9 for Phase I-E-2. Samples of approximately

500 - 850 mL total volume were collected on a weekly basis. The valves were opened automatically by a timer, usually every four hours. At that moment a total of 12 - 19 mL of water flowed from the sample point to a glass reservoir in one of two refrigerators located close to the sample point. The conduit for the samples was 1/8" i.d. black Teflon tubing. A minimum length of tubing was used so that the dead volume would be minimized (2.5 mL/linear foot).

Composite samples were used to determine Total Organic Carbon (TOC), Trihalomethane Formation Potential (THMFP), UV Absorbance at 254 nm, Color, pH, Conductivity, and in Phase I-E-2 Non-Purgeable Total Organic Halogen.

Discrete Sampling

At the time composite samples were taken and new bottles placed in the refrigerators, discrete samples were also taken for analysis of Inorganic Carbon, Dissolved Oxygen, Ammonia Nitrogen, and Nitrate. These analyses were run on site in the laboratory building of the T. L. Amiss Treatment Plant of the City of Shreveport, Louisiana. The following instruments were utilized for water quality parameters; figures in brackets refer to Method numbers in EPA publications (60):

pH: Orion 901 meter with combination electrode; standardization with standard commer-buffer preparations [150.1]

NH₃ Nitrogen: Orion 901 meter with Model 95-10 ammonia electrode (detection limit reported at 0.001 ppm N) [350.3]

Nitrate: Orion 901 meter with Model 93-07 nitrate electrode (detection limit reported at 0.1 ppm N)

Specific Conductance: Laboratory conductivity meter at T. L. Amiss plant laboratory [120.1]

Color: Visual method [110.2]

Dissolved Oxygen: Orion 901 meter with Model 97-08 oxygen electrode, samples analyzed immediately after taking [360.1]

UV: Beckman or Varian/Cary absorption spectrophotometer at 254 nm, with correction for turbidity at 600 nm.

TOC: Dohrmann Model DC-54 analyzer [415.1]

Inorganic Carbon: Dohrmann Model DC-54 analyzer, samples analyzed immediately after taking.

THMFP: Compositated water samples were transferred to duplicate 25 mL vials so that no headspace was present. Vials were capped with Teflon-lined rubber septa and sealed. Samples were chlorinated at a dose of 20 mg/L at a phosphate buffered pH of 6.5 and stored at 26°C (±2°C) for

three days. Excess sodium sulfite was added and the THM's analyzed by a pentane extraction procedure described by Glaze et al. (61). The ratio of pentane to water is 20:1, and the procedure involves removing 5 mL of water and adding one mL while keeping the bottle closed. Gas chromatography for analysis of THM's uses a 9' x 2 mm i.d. glass column with 10% squalane on 80/100 Chromasorb W/AW. A Hewlett-Packard Model 5840 GC with linearized Ni⁶³ detector is used. The pentane may be replaced with hexane, but in either case an internal standard 1,2-dibromoethane is present at approximately 100-200 ng/ μ L. Samples are shaken on a vortex shaker for 30 - 60 seconds for extraction.

Dissolved Ozone Concentration: The method of Bader and Hoigné was used (62). Since the trisulfonate salt of indigo was not available the disulfonate was used with no apparent problems. The extinction coefficient of indigo was taken from Bader and Hoigné (62).

Calibration and Quality Control Procedures

In general good laboratory practices were maintained. Glassware was washed before use with detergent, rinsed with purified water and dried at 130°C in a laboratory oven. All samples were run in duplicate, including duplicate chlorinations for THMFP. Instruments were calibrated at each time of use according to the manufacturer's directions and the analytical method being used. For GC runs, a methanol primary standard solution was prepared according to EPA protocol (63) and used to prepare calibration standards whenever GC work was to be done. Calibration standards were not kept for longer than one day, and methanol primary standards were kept about one month. Calibration runs were run in duplicate at the beginning of an analysis and were required to be within 10%. Calibration was repeated every twenty samples run. Reproducibility of duplicate samples for THMFP was usually within $\pm 10\%$.

The TOC analyzer was calibrated with potassium acid phthalate according to the directions of the manufacturer (Dohrmann Envirotech). Reproducibility of duplicate samples was usually within $\pm 5\%$. Inorganic carbon was run using the feature of the DC-54 which by-passes sample catalytic oxidation and analyzes only the gas purged after acidification of the sample. TOC samples were not chlorinated and had essentially no volatile organics which would have interfered with CO₂ measurements.

For standard water quality parameters similar calibration procedures were used as required by EPA protocols (60, 64).

Measurement of Operating Parameters

Various parameters were monitored throughout the pilot plant's operation.

Temperature--

After several measurements of water temperature through the treatment process with no noticeable temperature differences, the temperature at one site, the Waterboy flocculation chamber, was chosen to be monitored.

Turbidity--

Two Great Lakes flow-through turbidimeters were used to monitor the coarse-filtered raw water (TU1) and the Waterboy unit effluent (TU2). The turbidimeters were standardized monthly and their cuvettes were cleaned at least weekly.

Chemical Feed Rates--

Alum--The alum feed to the Waterboy unit is controlled by a small metering pump that feeds a concentrated alum solution at a constant rate. The alum feed rate (ALU) was found by measuring a timed quantity of this solution.

Ozone Feed Rate--The ozone concentration of the feed gas (oxygen) was found by shaking a known quantity of the gas with a known quantity of buffered indigo reagent and colorimetrically measuring the bleaching effect at 600 nm. This concentration multiplied by the oxygen feed rate (OXY) and divided by the diffuser water flow rate (F2) gives the ozone feed rate (OX).

Ozone Utilized--The efficiency of ozone transferred to water in the diffuser was determined by measuring the ozone feed rate (above) and the ozone concentration in the exhaust gas (by a similar procedure). The ozone utilized minus the residual ozone in the water leaving the diffuser gave the ozone demand. Typical values of ozone utilized were around 80% to 90% and ozone demand after 37 minutes retention time was complete. That is, ozone residuals in the water after 37 minutes were barely detectable.

Oxygen Feed Rate--The oxygen feed rate (OXY) was read from a floating-ball type flow meter incorporated in the ozone generator.

Air Feed Rate--The air feed rate (AIR) was found by diverting the diffuser exhaust to an inverted water-filled container and measuring the rate of water displacement. The oxygen feed rate was then subtracted from this value.

Volt--This is the value of the voltage controller of the ozone generator. It has a range of 0-10.

pH--The pH of samples of the coarse filtered raw water (pH1) and the Waterboy effluent (pH2) was found in the lab.

Flow Rates--The flows of the pilot plant were measured with turbine-type flowmeters until mid-summer 1980. For the remainder of the project, flows were measured manually by timing the filling of a gallon container. Flow rates were reported for the raw water (F1), the ozone diffuser (F2), column 1 (F3), column 2 (F4), and column 5 (F5).

Column Pressures--The pressures at the top of each column were measured with a dial-type pressure gauge, CPl-6 corresponds respectively to columns 1-6.

MICROBIOLOGY: METHODS AND PROCEDURES

Sampling Schedule

Once a month during the period January-November 1980, water and GAC samples were collected from the BAC pilot plant. Water samples were taken before and after each experimental carbon column and GAC samples were taken from sampling ports in the middle of each column (figure 8). These samples were immediately transported (on ice) to laboratories at North Texas State University (NTSU) in Denton, Texas where microbiological analyses were conducted. During the latter part of August, September and October 1980, additional samples of GAC were shipped on ice via express bus to NTSU in order to provide more bacterial data on the carbon itself. Beginning in mid-November 1980, column numbers 1 and 2 were deleted from the regular sampling routines as they were modified for further use in the Phase I-E-2 portion of the BAC project. However, all other columns continued to be monitored, as before, through July 1981.

Procedures

Several different analyses were used to describe microbiological activity on GAC. These analyses and their function are presented below.

1. Adenosine Tri-Phosphate (ATP) Assay-quantifies total viable microbial biomass present at the time of ATP extraction.
2. Modified Total Plate Counts (MTPC) - another but less sensitive quantification of bacterial populations. Also allows for microbial identification through various isolation techniques.
3. Coliform Assays - a bacterial group of organisms used as a general indication of possible contamination of samples by other pathogenic organisms.
 - a) Total Coliforms - first isolation step in the coliform assay to test for coliform presence.
 - b) Fecal Coliform - second isolation step in the coliform assay to test for coliform groups specific to fecal contamination.

ATP Assays

The validity of using the ATP assay as a measure of microbial biomass is based on two general assumptions:

1. That ATP is present in all living organisms.
2. That ATP is not readily available in its free form in the environment (i.e. pure ATP by itself is not found in the environment).

Assuming these two assumptions are correct, the following procedures for the extraction of ATP from water and carbon samples were employed.

Water Samples

One liter water samples were collected before and after each set of columns in bottles rinsed with water from the appropriate sampling points. These samples were then taken back to the laboratory (on site or at NTSU), subdivided into 250 mL aliquots, and extracted for 3-5 minutes each in a boiling buffer. During the first eight months of the study ATP extractions were performed only on the influent and effluent waters of a GAC column set. These extractions were performed using a Tris buffer (Tris (hydroxymethyl) aminomethane) at a pH 7.71 and having an extraction efficiency of greater than 85% (65). When it became apparent that the measurement of microbial populations on the GAC itself were crucial to the attainment of the project goals, a literature search was implemented to find a high efficiency extraction medium to obtain ATP from the GAC particles (extraction of ATP from the GAC using Tris buffer only ranged from 3-30%). In a report by Bulleid (64) on extracting ATP from marine sediments, several extracting mediums were tested. A sodium phosphate/citrate buffer termed McIlvaine buffer was found to have extraction efficiencies of greater than 90% for sediments. Taking his results into consideration similar tests were performed (see Table 2) substituting GAC for sediments and obtained extraction efficiencies of ATP from GAC of approximately 90%. In addition the McIlvaine buffer provided slightly better extraction efficiencies than the Tris buffer for liquid samples. Therefore, it was decided to use only one buffer, the McIlvaine buffer, to help minimize variances caused by buffer difference during data generation.

Carbon Samples

Carbon (GAC) was taken from the middle sampling port (see figure 8) using a spatula to transfer it to 75 mL presterilized brown glass vials. At various times it was possible to obtain the carbon by letting it flow out of the sampling port using water under low pressure. The samples were then transferred to the laboratory where three 2 mL (packed volume) portions of GAC were extracted for 10 minutes each (extraction time determined from figure 10) in boiling McIlvaine buffer at a pH of 7.71. The extractions were performed on hot plates using 150 mL beakers covered with watch glasses as the extracting vehicles. After extraction, each extract was centrifuged for 5 minutes at 3,000 rpm (Damon Spinette model, IEC, Centrifuge) in order to remove any carry over particulates that might have been present in the extract. After centrifugation, each extract was diluted to a constant volume (10 mL in this study) in a test tube and then frozen until final analysis.

Analysis of ATP Extracts

The frozen ATP extracts were analyzed for ATP content in the following manner. A standard ATP solution of 100 ng mL^{-1} ($.2 \text{ mL} = 20 \text{ ng ATP}$) was made by diluting di-sodium ATP crystals (12.3 mg l^{-1}). This solution was divided into 1 mL fractions which were frozen until use. Crude lypholized luciferin-luciferase enzyme (from Sigma Chemical Company) was hydrolized with Tris buffer (0.2 M; pH = 7.75) approximately 20 hours

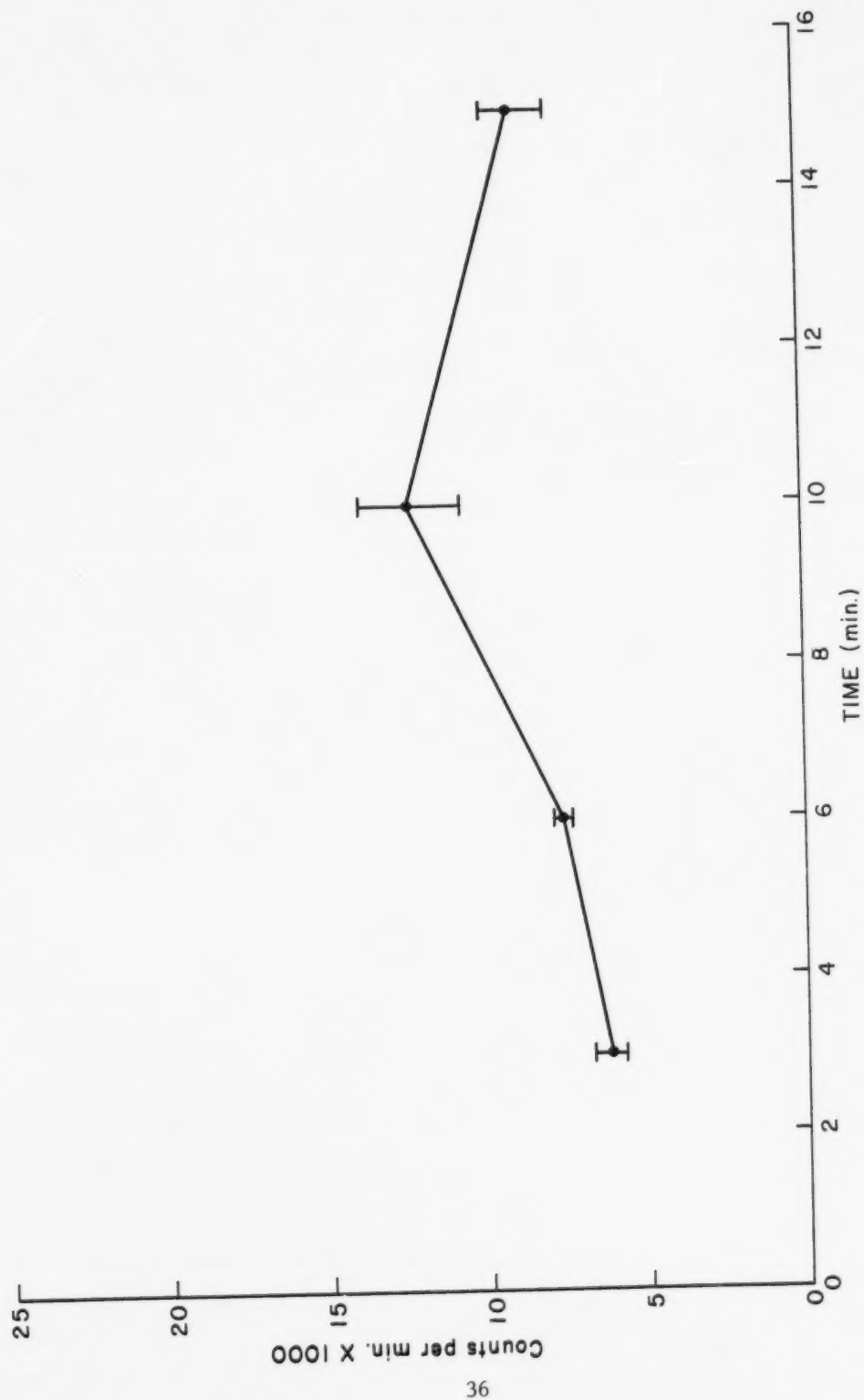


Figure 10. ATP Extraction Efficiency as a Function of Time of Extraction.

TABLE 2. CALCULATION OF PERCENTAGE RECOVERY OF ATP FROM GAC USING McILLVAINE BUFFER (66)

ATP (ng) in spiked GAC extract (10 mL)	Extracted GAC dry wt. (grams)	Est. ATP (ng/g) on GAC alone	ATP (ng) recovered from bacterial spike
(A)	(B)	(C)	(A) - (C)
84.5	1.96	76.8	7.7
86.3	2.05	75.5	10.8
86.7	2.10	77.9	8.8
88.3	1.89	74.7	8.6

$$\bar{X} (A) - (C) = 8.97 \pm 1.3$$

ATP content in the bacterial spike (1.0 mL) = 9.8 ng/L

$$\therefore \text{percentage recovery } \frac{8.97}{9.80} = 0.915 \times 100 = 91.5\%$$

before use. After aging three to four hours at room temperature (22-24°C) the enzyme suspension was centrifuged 20 minutes (3200 rpm) at room temperature, the supernate decanted, and allowed to stand at room temperature for the remaining 16 hours.

Analyses of the extracts and standards were made using a Model 2000 ATP Photometer, JRB Company. A 0.20 mL aliquot of extract (i.e. of sample or standard) was placed in a scintillation vial. As an equal aliquot of enzyme was added to the liquid in the vial, the photometer was activated. Following a 15 second delay, the vial was placed into the counting chamber. The instrument integrated a one minute portion of the decay curve and a digital (LED) readout was produced (see Holm-Hansen) (65). Concentrations of ATP in extracts were calculated from least squares linear regression of data generated from assay of ATP standards. Since a crude enzyme of variable activity was utilized, a fresh set of standards was prepared prior to analysis of each set of extracts. Background assays of the enzyme and occasional sample spikes were performed on the samples to maintain quality control. For the determination of ATP levels on GAC, packed carbon readings (in mL) were converted to concentrations of ATP per gram dry weight of carbon via a standard curve (figure 11) developed specifically for this project.

Modified Total Plate Counts

Water samples for modified total plate count (MTPC) were taken from three way solenoid operated sampling valves located before and after each carbon column (see figure 8). Samples were sealed in 500 mL presterilized glass containers with screw cap lids and transported back to the North Texas State University Laboratories on ice. All samples were processed within 24 hours. Samples of activated carbon for MTPC were obtained from the middle sampling port of each GAC column in the same manner as for the ATP samples. The GAC samples were then put on ice and shipped with the water samples.

Elution of Microorganisms from GAC

In order to maximize the recovery of microorganisms from the GAC surfaces, the samples were subjected to sonification (Sonifer cell Disruptor, Model W185D; Heat Systems-Ultrasonics, Inc., Plainview, L.I., N.Y.) as recommended by McElhaney, *et al.* (67). One mL of the wet GAC was placed in a sterile, graduated 10-mL cylinder; a mL of sterile, pH 7.0 phosphate buffer was added. This suspension was then transferred to a sterile 50 mL beaker for sonification. The sonifier probe was disinfected with 75% alcohol and the carbon suspension was then sonicated in an ice bath for one minute at 60 watts of energy. As soon as possible (<1 hour), the cold sonicate was analyzed microbiologically, both quantitatively and qualitatively.

Quantitation of the GAC Microbial Population

The basic procedure for "total plate counts" was modified from that described in "Standard Methods for the Examination of Water and Wastewater"

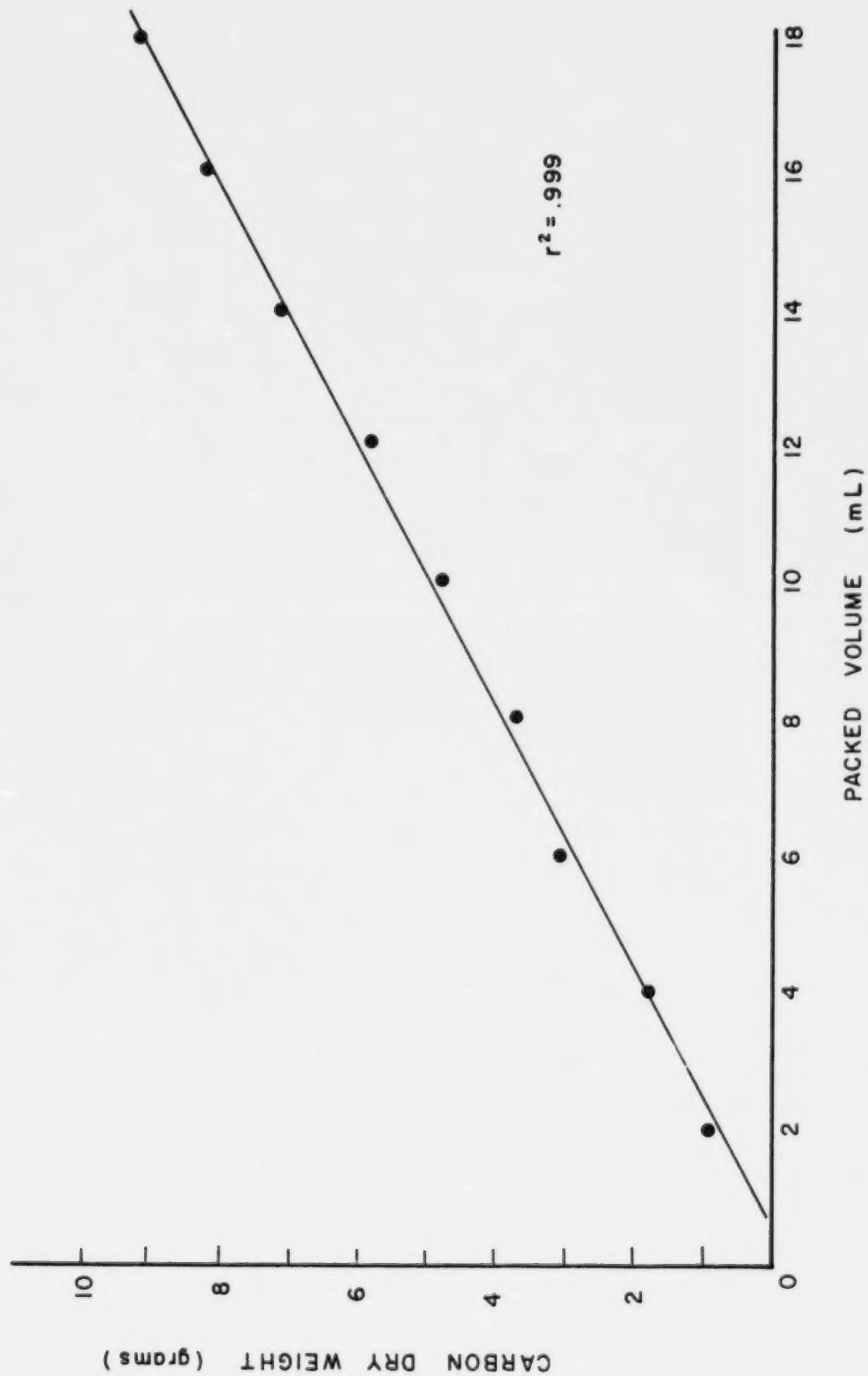


Figure 11. Relationship Between Wet Packed Volume and Dry Weight of Granular Activated Carbon (Filtrisorb - 400).

(68). Based upon the recommendations of McElhaney, soil extract agar (SEA) (Table 3) was employed. Serial decimal dilutions of the sonicate or the influent-effluent water were prepared in 16 x 150 mm test tubes containing 9 mL sterile phosphate buffer. One mL of each dilution of the samples was transferred to each of two sterile petri dishes (100 x 15 mm) and mixed thoroughly with 15 mL of melted (45°C) SEA. Other petri dishes were prepared with selective media, viz: McConkey Agar (Difco), Pseudomonas Isolation Agar (Difco), Burke's 1% Glucose Agar and Cooke's Rose Bengal Agar with tetracycline (0.035 mg/mL). These plates were inoculated in duplicate with 0.1 mL of undiluted or diluted samples. The inoculum was spread evenly over the agar surface with a sterile, bent-glass rod (alcohol-flamed). In addition, Actinomycetes Isolation Agar (Difco) with actidione (0.05 mg/mL) was inoculated by the double-layer technique as described in "Standard Methods". The function of each medium and the technique of inoculation are shown in Table 4. All plates were inoculated in duplicate and then inverted and promptly incubated at 28°C for seven days; Actinomycetes Isolation Agar was incubated for 14 days. All counts were extrapolated from the most countable pair of plates and expressed either as the number of colony-forming units per mL of sample or colony-forming units per gram dry weight of carbon.

Identification of Microbial Isolates from BAC

After seven days of incubation, the SEA plates were examined under a stereoscopic microscope (20X magnification) to determine the dominant colonial types. Pure cultures of the dominant colonies were isolated on streak plates of nutrient agar (Difco) and transferred to nutrient agar. Isolates were maintained on slants. All isolates were stained by Gram's method and processed according to the basic determinative scheme displayed in Figure 12. Identification to the generic level for bacterial isolates was facilitated by: (1) Bergey's Manual of Determinative Bacteriology; (2) Practical Clinical Microbiology and Mycology Techniques and Interpretation; (3) Manual of Clinical Microbiology; (4) Computer Coding and Identification System for OXI/FERM Tube (Roche Diagnostics, Division of Hoffmann-LaRoche Inc. Nutley, N.J.); (5) Manual for the Identification of Gram-Negative Nonfermentative Organisms. Bergey's Manual was the final arbitrator for all identifications.

The Recovery Rate of Pseudomonas Isolation Agar.

Because Difco's Pseudomonas Isolation Agar (PIA) was designed for isolating Pseudomonas from industrial materials such as cosmetics and lotions and because the counts obtained in the medium were exceedingly low, it is possible that many aquatic pseudomonas found in the higher dilutions of the SEA plates were unable to grow in this medium. Therefore plate counts of young (2 hr.) nutrient broth cultures of Pseudomonas aeruginosa, P. fluorescens and P. stutzeri (all from the Department's Stock Culture Collection) were made in both the Pseudomonas Isolation Agar and nutrient agar using the drop plate method. Plates inoculated with dilutions of cultures of P. aeruginosa and P. stutzeri were incubated at 37°C; those inoculated with P. fluorescens were incubated at 26°C. The recovery rate was then estimated by calculating the ratio of the number of

TABLE 3. PREPARATION OF SOIL EXTRACT AGAR (SEA)

Nutrient Agar (Difco)	750 mL
-----------------------	--------

Soil Extract*	250 mL
---------------	--------

Adjust pH to 7.0

Sterilize (121°C, 15 min.)

*Add 385 g "African Violet soil" to 1 liter of distilled water containing 0.1% NaCO_3 ; autoclave the suspension at 121°C for one hour and filter it through Whatman No. 1 paper. Store in screw-capped bottles at 4°C until needed.

TABLE 4. SELECTIVE MEDIA AND TECHNIQUES USED FOR ISOLATION OF DIFFERENT BACTERIAL GROUPS

	McC.*	Actino.*	Pseudo.*	Burke's*	Cooke's*
Technique	Spread Plate	Double Layer	Spread Plate	Spread Plate	Spread Plate
Incubation Time, days	7	14	7	7	7
Incubation Temperature, °C	28	28	28	28	28

*McC. = McConkey Agar: certain gram negative organisms.

Actino. = Actinomycetes Isolation Agar with actidione: Actinomycetes.

Pseudo. = Pseudomonas Isolation Agar: certain Pseudomonas species.

Burke's = Burke's 1% Glucose Agar: free-living, nitrogen-fixing bacteria.

Cooke's = Cooke's Rose Bengal Agar with tetracycline (pH 4.5):

most fungi.

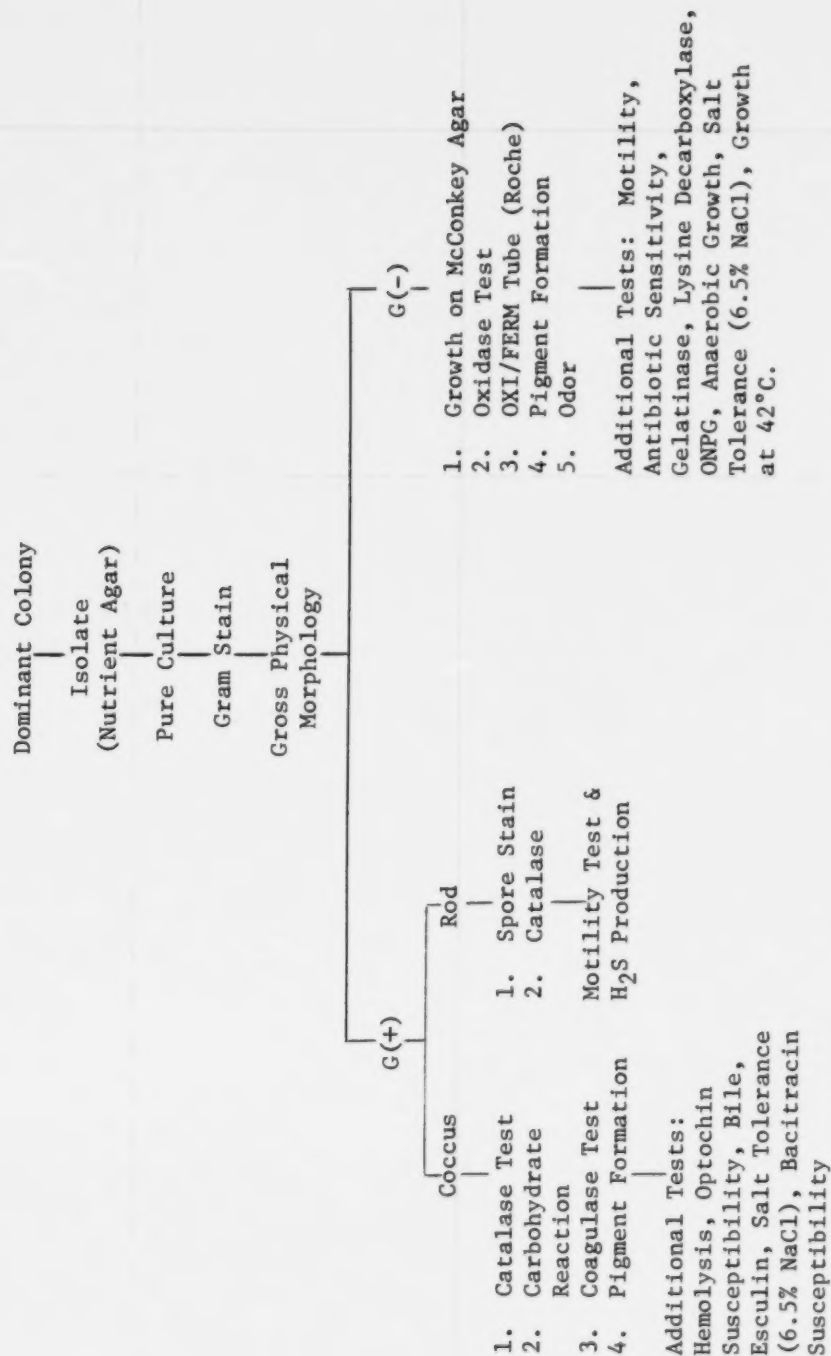


Figure 12. Flow Chart for Bacterial Identification.

CFUs/mL as determined on the Pseudomonas Isolation Agar to the number of CFUs on nutrient agar.

Coliform Tests

Total and fecal coliform tests were conducted utilizing the same water samples from which MTPC and bacterial isolates were taken. Colony densities were calculated according to the membrane filtration method outlined in "Standard Methods" (68) and from EPA document No. 600/8-70-017 (69).

SECTION 6

PILOT SCALE EVALUATION OF THM PRECURSOR REMOVAL RESULTS AND DISCUSSION

OBJECTIVES

The principal objectives of the pilot project were as follows:

1. To test on a pilot scale the following unit processes for the removal of THM precursors in a southern U.S. reservoir high in natural organics:
 - a. traditional treatment including coagulation, sedimentation and rapid mixed-media filtration.
 - b. ozonation in a turbine contactor with short contact time, followed by a longer residence time in contact with residual ozone.
 - c. granular activated carbon adsorption in packed beds operated in a downflow mode (pressure GAC filters).
2. To determine the populations of bacteria in the GAC filters, and the role these bacteria play in the removal of organic substances vis á vis pure adsorption processes.
3. To evaluate the capital and operating costs for the addition of GAC filters to typical southern U.S. water treatment plants such as those supplied from the source of water for this study (Cross Lake, Louisiana).

RESULTS

The pilot plant study was divided into two operational phases:

Phase I-E-1 [December 29, 1979 - March 13, 1981]

Phase I-E-2 [March 24, 1981 - July 23, 1981]

During Phase I-E-1, the pilot plant consisted of the treatment trains shown in Figure 7. At the onset of Phase I-E-2, GAC columns 1, 2, 7 and 8 were repacked, two with GAC and two with sand. GAC columns 3, 4, 5 and 6 were left in place and continued to operate until the end of the project. These four columns, two receiving unozonated water (5 and 6) and two receiving ozonated water (3 and 4), provided the bulk of the data

for the pilot phase of this project.

Therefore, in this section data from columns 3, 4, 5 and 6 for the entire project period will be discussed in detail. As a necessary introduction, data relating to treatment prior to the GAC columns will also be discussed. This pretreatment consisted of alum flocculation, tube settling, mixed-media filtration and ozonation. Data from columns 1 and 2, which were operated only for approximately four months will also be discussed in this section.

Following this discussion the results obtained from samples taken in Phase I-E-2 from the other four columns will be analyzed. These columns which were labeled numbers 9, 10, 11 and 12 are diagrammed in Figure 9. The data base for these columns is less extensive than for columns 3, 4, 5 and 6, but some important conclusions may be drawn from it.

Effect of Coagulation - Mixed-Media Filtration

The principal purpose of the Neptune-Microfloc Waterboy pretreatment unit was to provide settled-filtered water of low turbidity for the remainder of the pilot plant. The Waterboy utilized alum flocculation at a dose of approximately 50 mg/L. No attempt was made to optimize or systematically vary this dose, the only criterion being to produce water with less than one standard turbidity unit. Nonetheless, the data accumulated by analysis of samples taken before and after the Waterboy provide useful information on the effect of coagulation and mixed-media filtration on THM precursors.

Figures 13 and 14 show THMFP and TOC values of the lake water and settled-filtered water from the Waterboy. Lake water was actually taken at the entrance to the pilot plant trailer, approximately one thousand linear feet from the intake point in the lake. At normal flow rate (10 GPM) this represents a residence time of approximately sixteen minutes between lake and trailer.

The top curves in both Figures 13 and 14 show the variation in THM precursors and total natural organics respectively in the lake water. A seasonal variation is apparent in each figure although it appears higher THMFP values were present in the summer of 1981 as compared to summer of 1980. It should be noted that the summer of 1980 was considerably drier than 1981; the lake was near conservation level in 1980 and nearly full in 1981.

The lower curves in Figures 13 and 14 show values for settled-filtered water, that is, the product water from the Neptune-Microfloc Waterboy package treatment plant. For the period of study the Waterboy was operated without preoxidation, so the removal in the unit is due only to alum flocculation with tube settling followed by rapid mixed-media filtration. Figures 13 and 14 show that the seasonal fluctuation of both TOC and THMFP seen in the lake water (top curves) is damped in the Waterboy product (lower curves). It appears that the natural organics responsible

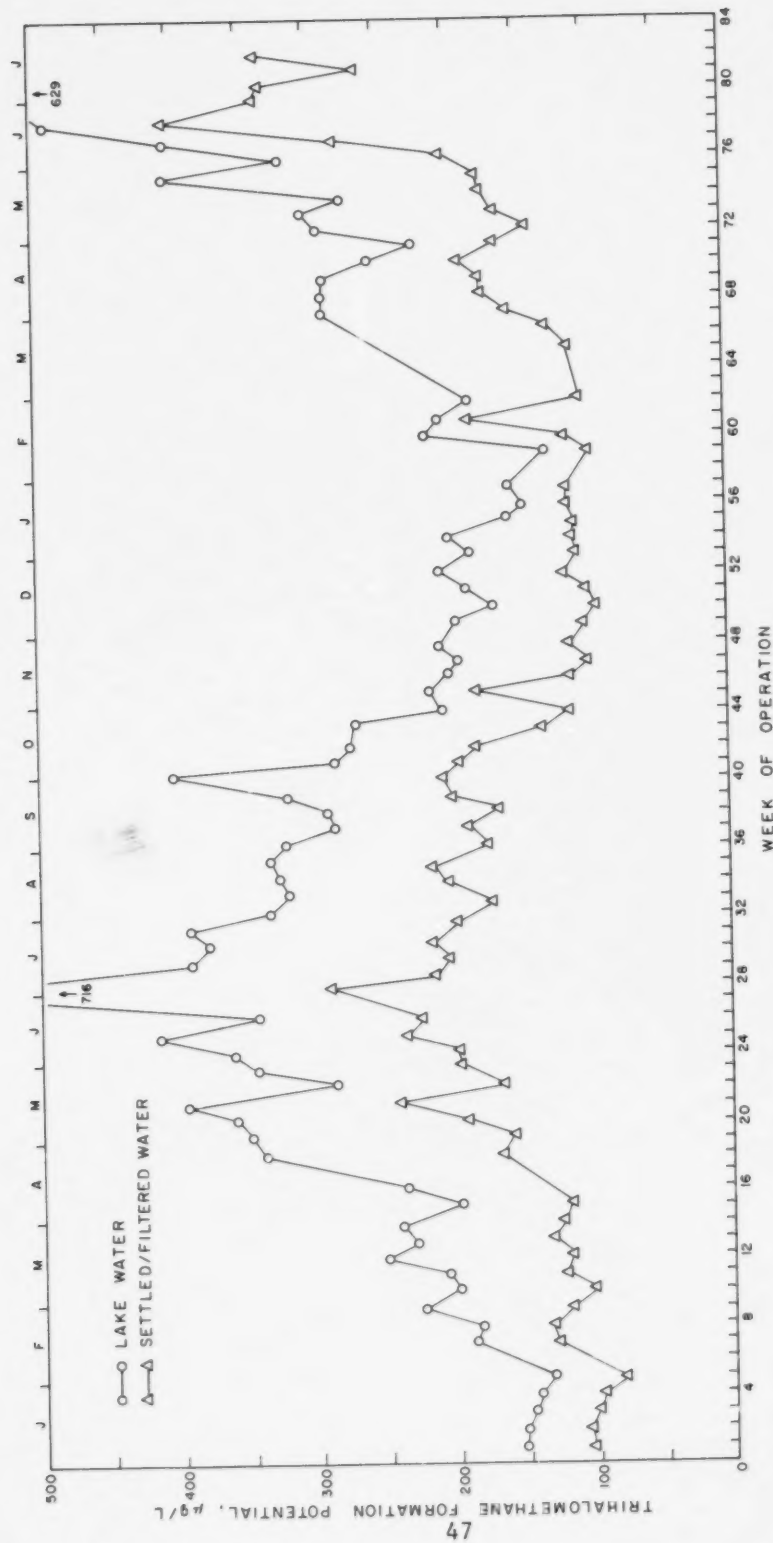


Figure 13. Trihalomethane Formation Potential Values for Cross Lake Raw and Alum Settled - Filtered Water (20 mg/L Chlorine Dose at pH 6.5; 3 days incubation at 26°C).

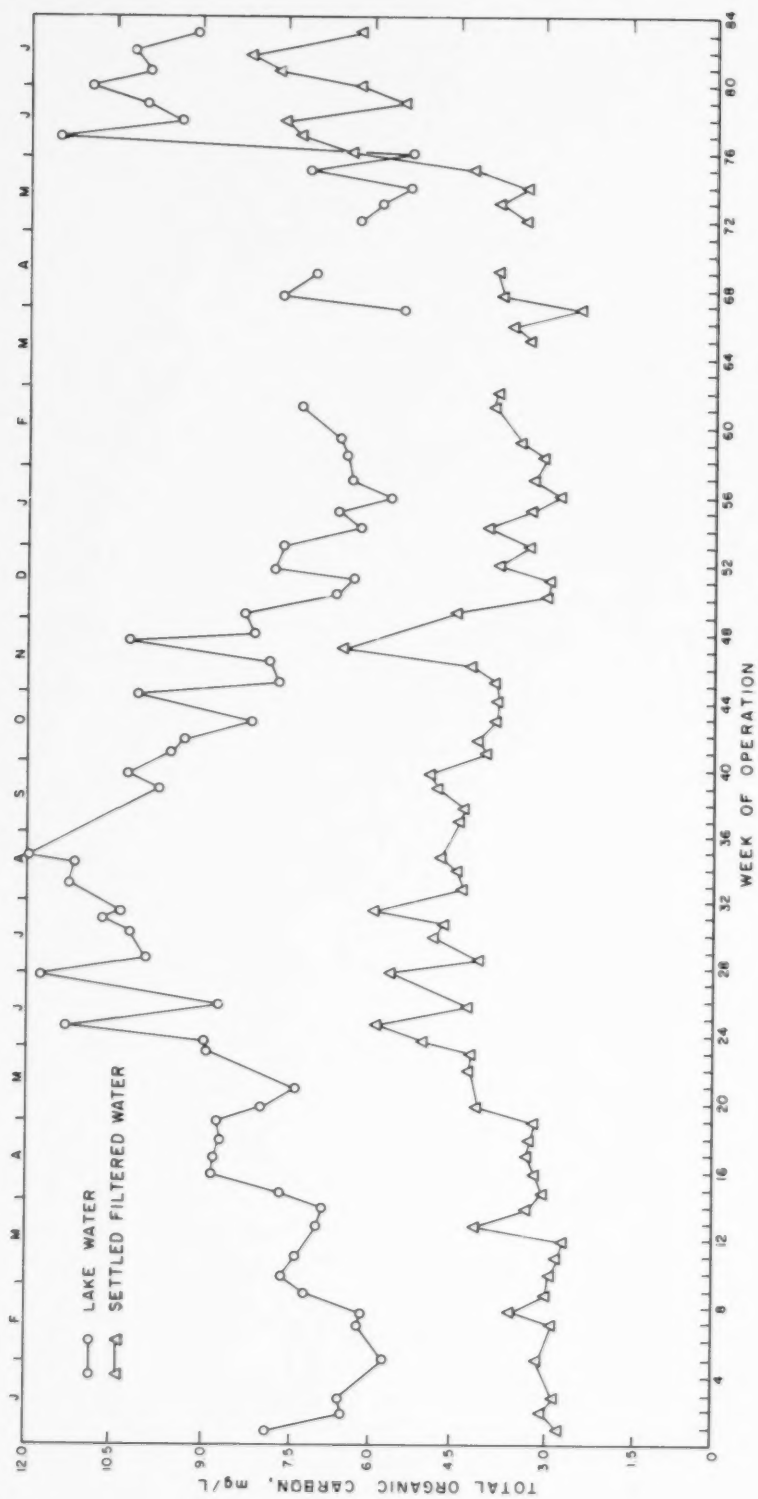


Figure 14. Total Organic Carbon Values for Cross Lake Raw and Alum Settled - Filtered Water.

for the large rise in TOC and THMFP in the warm months are more effectively removed by the Waterboy. The exception appears to be the summer of 1981 where high THMFP values were observed in the Waterboy product; however during this period the Waterboy was operating above rated capacity and probably at a loss of some efficiency. An analysis of the data plotted in Figures 13 - 14 indicates that the Waterboy removed approximately 40% of the THMFP and 50% of the TOC of the influent water. Again, there is a slight seasonal variation, with removal rates of THMFP averaging 35% ($\sigma = 6\%$) in the winter months of early 1980 (weeks 1-8) and the winter months of 1980-81 (weeks 45-60). In the spring-summer-fall periods of 1980 (weeks 17-44) removal is generally at a higher rate 44% ($\sigma = 6\%$). Overall removal of THMFP for weeks 1-60 is 40% ($\sigma = 7\%$). Removal of TOC is somewhat more efficient than for THMFP (52% average year-round), but the same trends are apparent. Percent reductions of TOC for weeks 1-16 and 45-60 are 56% ($\sigma = 7\%$) and 46% ($\sigma = 5\%$) respectively. For weeks 17-44 removals in the Waterboy averaged 54% ($\sigma = 6\%$).

These observations are generally in accord with other workers in the field who have studied alum flocculation as a means of reducing THMFP. Love and coworkers (19) found approximately 60% and 58% removal of TOC and THMFP respectively. The test medium was Ohio River water and treatment was similar to this work. These workers also point out that formation potential for brominated THM's is removed with less efficiency than chloroform potential. The same observation may be made in this work, as shown in figure 15. Apparently, bromide is not removed effectively by the Waterboy and is still available to form brominated THM's in approximately the same quantity after treatment (19).

As a final aside to this section, it should be recorded that the Waterboy operated almost unfailingly for the entire project period without preoxidation. Low turbidity water was produced consistently with an alum dose of approximately 50 mg/L, although preliminary testing showed that lower values sufficed for this purpose the majority of the time. This observation is important in view of the need to eliminate prechlorination as a means of controlling THM production, a modification which is opposed by some local authorities who contend that preoxidation is necessary for efficient flocculation-sedimentation. While this may be true under certain conditions it is not generally true as the pilot studies show.

Effect of Oxidation with Ozone

The oxidation of THM precursors with ozone has been the subject of investigations by Rook (70), Riley *et al.* (71) and Glaze *et al.* (29). All concur that ozonation may form precursors as well as destroy them. This is presumably due to formation of oxidation products which can act as THM precursors, for example methyl carbonyl compounds. This pilot study was designed to test a potential remedy to this problem, that is to use short ozone-precursor contact times. It is conceivable that precursors initially present (P_1) could be destroyed by ozone in a rapid ozone transfer-chemical reaction process carried out in such a way so as to minimize production of secondary precursors (P_2). The method chosen

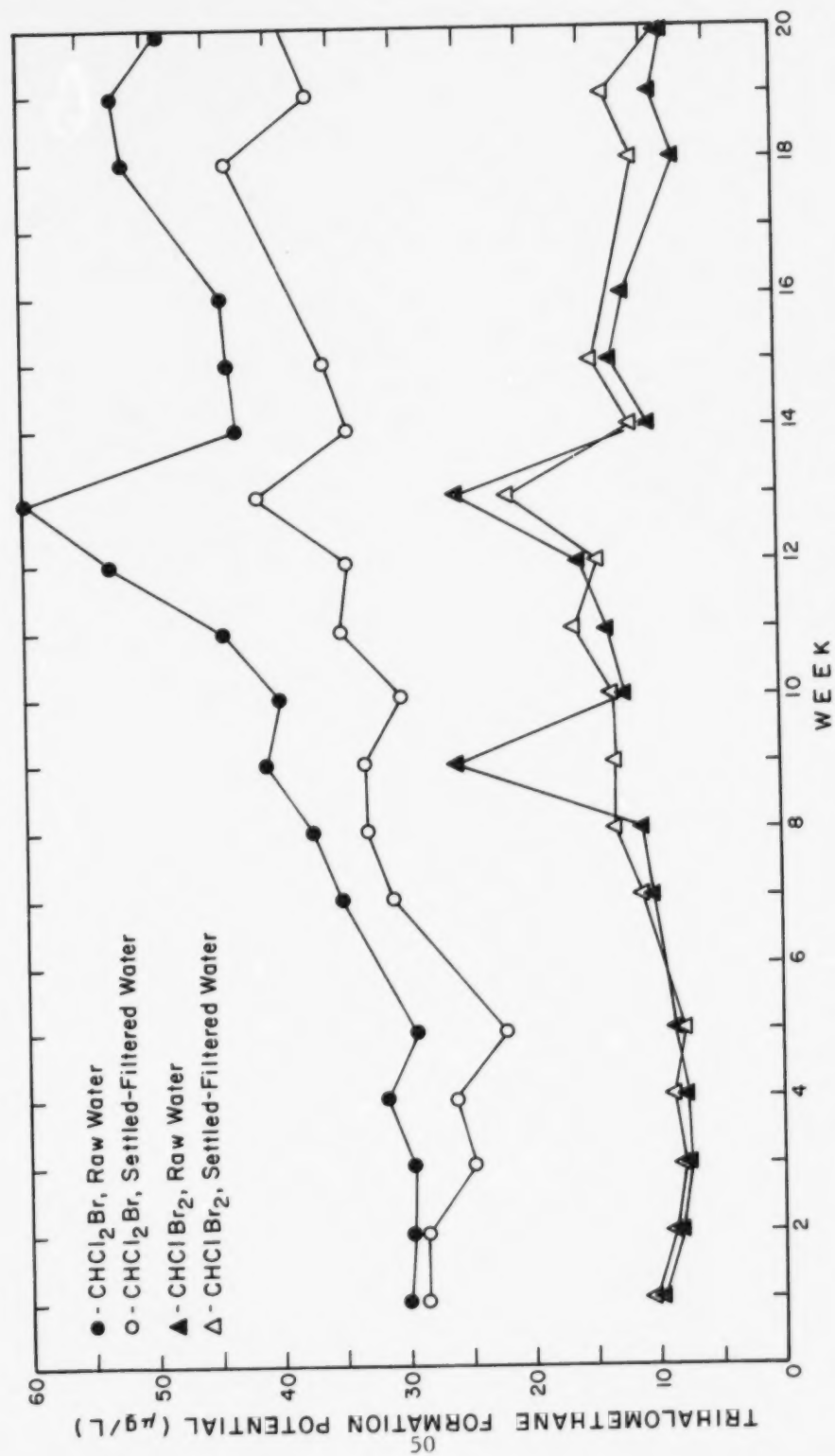


Figure 15. CHCl_2Br and CHClBr_2 Formation Potentials for Raw and Alum Settled - Filtered Water.

for this purpose was to use a turbine-style contactor (the Kerag type) followed immediately by a series of GAC columns. Activated carbon should serve to quench the ozone concentration which remains from the contactor, hopefully preventing reformation of secondary precursors. As a control to this test a second stream of water is diverted from the ozone contactor to a holding tank (the ozone detention basin). Water is held in this tank for a longer period*, during which conversion of natural organics to secondary precursors could presumably occur. The stream from the ozone detention basin is represented by sample point 12 while water directly from the contactor is taken at sample point 9.

Figures 16 and 17 show TOC and THMFP values at sites 9 and 12 as compared to site 5, the effluent from the Waterboy holding basin. It is clear that there is little significant difference between water which has seen ozone for a short or a long contact time. Whether this obviates the assumptions discussed in the previous paragraph is not known at this time; however, it is possible that the operational conditions of the pilot study precluded a fair test of the assumptions. More specifically, it should be noted that this study intentionally used ozone doses which were not "excessive". As discussed earlier, the ozone doses used were in the range of 2.0-6.3 mg/L, never enough to give more than a few tenths of a part per million ozone residual at the exit of the turbine contactor. This choice was made in order to test ozonation conditions which were judged to be realistic; i.e. without unacceptable capital and operating costs. These doses were insufficient to leave a large residual of ozone in the water after initial contacting, presumably a prerequisite to P₂ formation. Even during the first few weeks of testing when the ozone dose was 6.3 mg/L ozone residuals at site 9 were only approximately 0.5 - 0.8 mg/L. Thus, secondary precursor formation was not encouraged, and it is unlikely that this project has adequately tested the hypothesis suggested earlier. In any case, Figure 17 shows that oxidation with ozone is not a good method for the removal of THM precursors in natural waters such as Cross Lake. Throughout most of the test period ozonation at the doses used had a barely perceivable effect on THMFP. During the summer period of 1980 the effect is greater than in other periods, but even during this period THMFP was reduced only 10 - 15% by direct oxidation. Clearly, ozonation per se is not a preferred unit process for THM precursor control, albeit some oxidation of active sites is affected by ozone (68).

Figures 16 and 17 show the very high values of TOC and THMFP observed in the Waterboy product during the months of June and July of 1981. The effect of ozone during this period was greater than during earlier periods with the decrease in THMFP averaging 20%. This enhanced effect may be due to a change in the nature of the organics in the lake; however, as noted earlier the Waterboy was being operated above capacity during this period. Therefore, the observed effect may be due to enhanced coagulation in the ozone contactor and detention basin, although no

*In Phase I-E-1 retention time in the ozone detention basin was 37 minutes. In Phase I-E-2 retention time was reduced to 25 minutes, but in either case ozone residual after detention was very low (<0.1 mg/L).

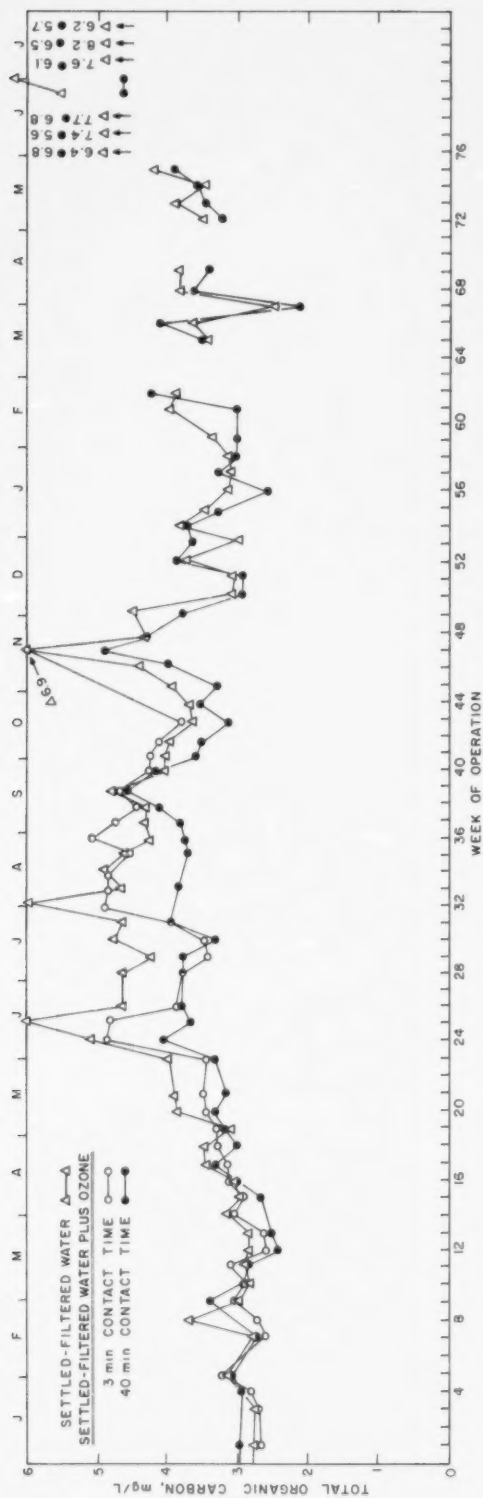


Figure 16. Total Organic Carbon Values for Ozone Treated Water at Sites 9 (3 min. Contact Time) and 12 (40 min. Contact Time).

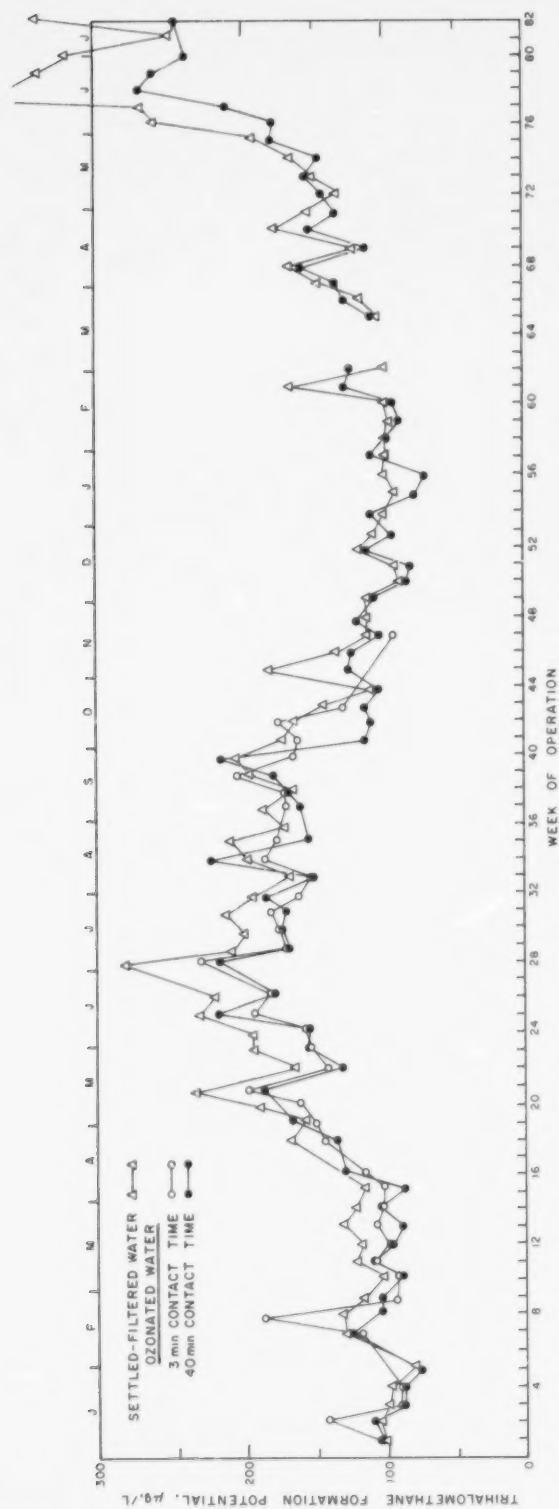


Figure 17. Trihalomethane Formation Potential Values for Ozone Treated Water at Sites 9 (3 min. Contact Time) and 12 (40 min. Contact Time).

examination was made to confirm this possibility.

In summary, ozonation is not a very effective method for the removal of THMFP from Cross Lake water after traditional treatment. However, as we shall note in the following section, the destruction of THMFP in the ozonation system, however small, is sufficient to make the Waterboy-Ozonator-GAC train outperform the Waterboy-GAC train over the long term of the project. An analysis of the costs associated with the addition of ozone is given in Section 7 of this report.

Effect of GAC Filters: Column Pairs 1-2, 3-4 and 5-6

At the outset of this section it should be recognized that the major objective of this project was to delineate and rationalize, if possible, the mechanisms by which granular activated carbon columns act to remove natural organic impurities in water. It is not clear if this objective has been realized although much has been learned of the process. The approach which shall be used in this section is as follows: the removal of TOC and THMFP in the GAC columns will first be discussed in empirical terms. Then an attempt will be made to rationalize these results in terms of adsorption and microbiological mechanisms. And finally, a summary statement will be made with respect to the feasibility of combined GAC adsorption - microbiological removal as a treatment process for THM precursor removal. In Section 7 an analysis of costs associated with O₃-GAC or GAC-only processes will be presented.

The key parameter used in this study is THMFP, that is the capability of the water produced to form trihalomethanes upon chlorination. The conditions used to determine THMFP in this work were decided after a laboratory scale study of THM formation after dosage of chlorine. These experiments showed that 20 mg/L chlorine would serve to chlorinate a sample of Cross Lake water having a TOC of 15 mg/L such that a residual of chlorine remained after exhaustion of the THM-formation potential. Moreover, under these conditions an incubation time of three days was sufficient to give the maximum yield of THM's, at least within experimental error of the determination. Thus, the following conditions were chosen for the determination of THMFP in this work.

Chlorine dose: 20 mg/L
pH: 6.5 (buffered)*
Temperature: 26°C ± 2°C (room temperature for Shreveport
Incubation Time: 3 days laboratory)

Experimental details are given in previous sections of this report.

Values of THMFP were determined according to this procedure for waters influent to and effluent from the GAC columns described earlier and

*A pH of 6.5 was used because it corresponded to the value chosen in work performed earlier in this and other studies. Although the pH in the Shreveport distribution system is nearer to 9.0 the lower value was continued in order to give continuity to the data base.

diagrammed in Figures 7 and 9. In addition various other parameters, chemical and microbiological, were determined simultaneously, providing the data base for the pilot plant GAC columns. These data are summarized in the following sections.

Chemical Parameters--

Figures 18, 19 and 20 show plots of THMFP influent to and effluent from the GAC columns receiving unozonated water (figure 18), ozonated water with ca. 3 minutes ozone contact time (figure 19), and ozonated water with 28-40 minutes ozone contact time (figure 20). Figures 21-23 are the corresponding plots for the GAC columns using the parameter TOC. Each of these plots shows the expected breakthrough of the first column after in-service times of 8-12 weeks. However, as others have noted (40-42) the breakthrough curve is not sharp, and what appears to be a period of pseudo steady-state removal occurs during the period from week 25 to week 44. The effect is more discernable in Figures 24-29 which show the same data plotted as the ratio of effluent to influent concentration. From these plots the pseudo steady-state region appears to be "flatter" for the GAC columns receiving ozonated water, but this may be statistically insignificant. In the pseudo steady-state net removal of TOC and THMFP is about 20% across the first column of a series (12 minutes EBCT) and 50% across the two column set.*

As noted above the pseudo steady-state period appears to terminate at approximately the 44th week of operation. During the period from week 44 to approximately week 52 gradual diminution of performance occurs. Then at week 52 precipitous decline in performance is observed and thereafter net removal across the two column set is erratic and seldom more than 25%.

It should be noted that week 44 is the last week of October and week 52 the end of the calendar (and operational) year. Water temperatures during this period were slowly declining as shown in Figure 30, and reached values below fifteen degrees the second week in November, week 46. Until the end of the first operational phase, week 63, temperatures were generally low, reaching twenty degrees again only in week 67, the first of April 1981. Thus, one is tempted to ascribe the second breakthrough during weeks 44-52 to a decline in microbiological removal mechanisms due to the onset of cold water temperatures. More discussion on this topic will be given in the following parts of this section.

During weeks 63-64 the pilot plant was replumbed for Phase I-E-2 as discussed before. Beginning at week 65 four new columns were started as shown in Figure 9. However, carbon columns 5-6 and 3-4 were continued as before, receiving settled-filtered and ozonated water respectively. It

*As shown in the figures carbon columns 1 and 2 were not monitored regularly after week 43. The test of long versus short ozone contact times had been completed by this time and no further value was derived from the continual monitoring of the columns with short ozone contact time.

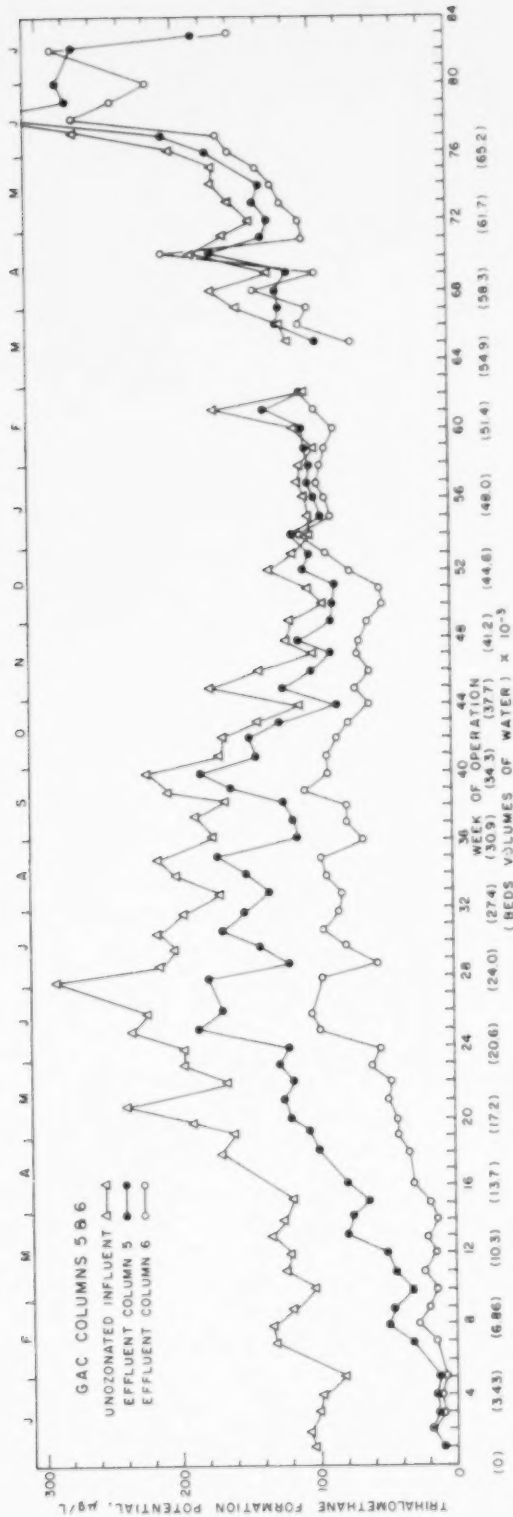


Figure 18. Trihalomethane Formation Potential Values for Settled - Filtered Water and Effluents of GAC Column Set.

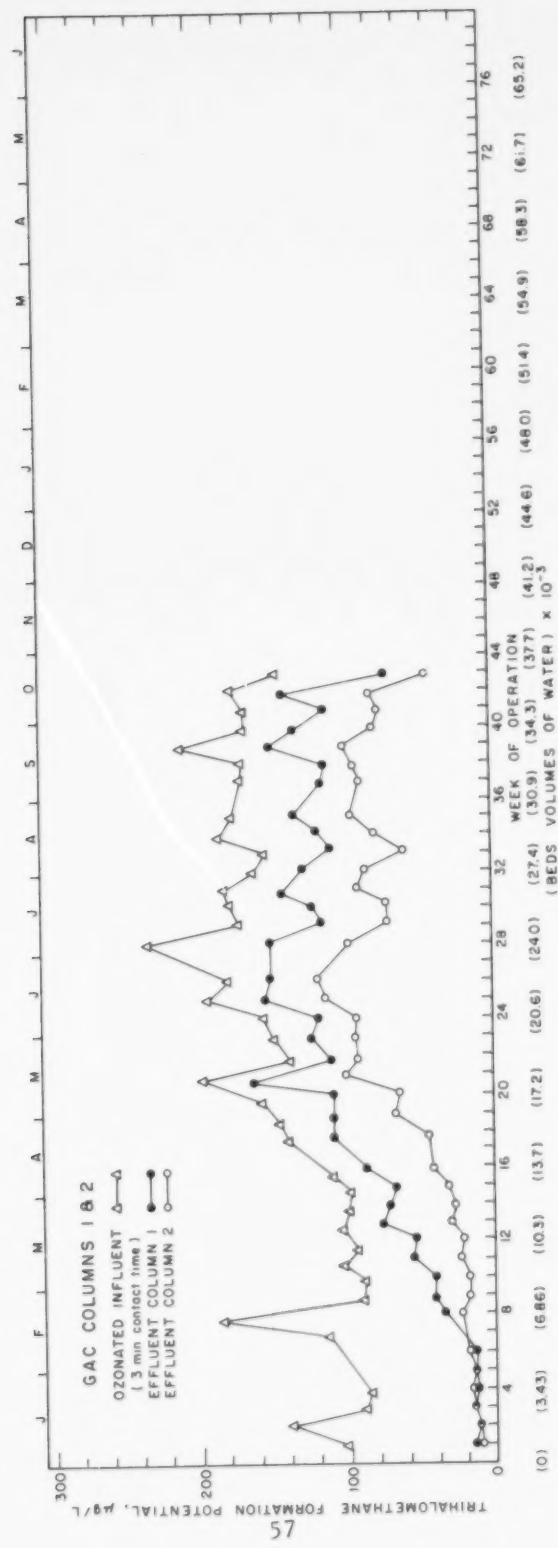


Figure 19. Trihalomethane Formation Potential Values for Short Contact Time
Ozone Treated Water and Effluents of GAC Column Set.

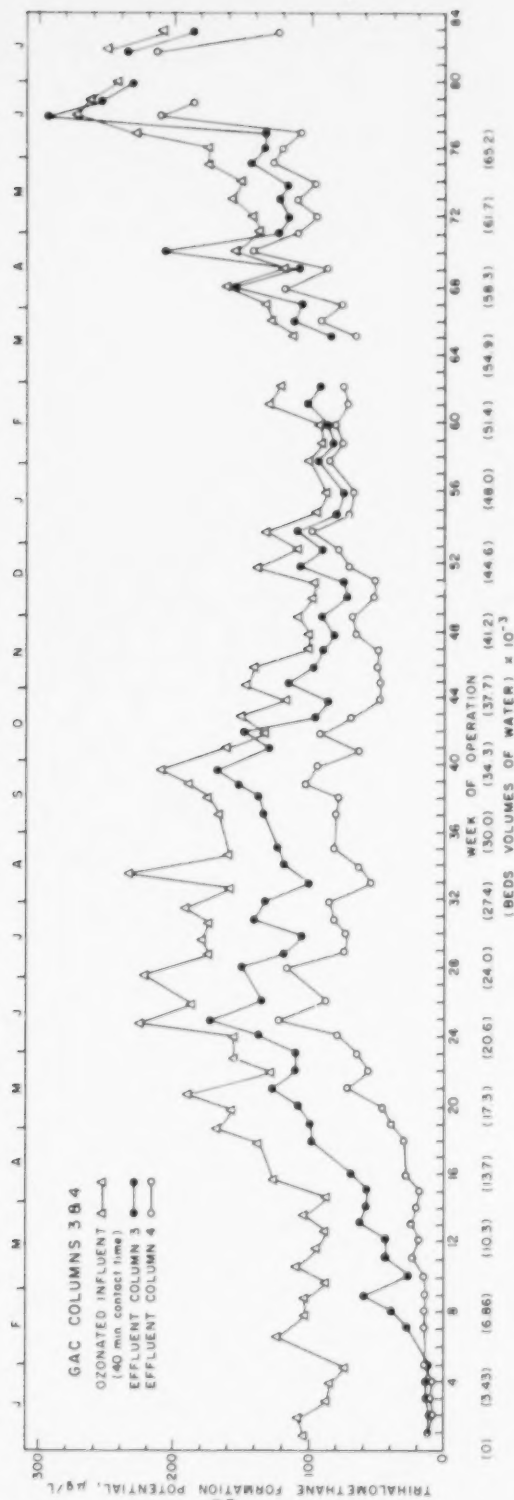


Figure 20. Trihalomethane Formation Potential Values for Long Contact Time Ozone Treated Water and Effluents of GAC Column Set.

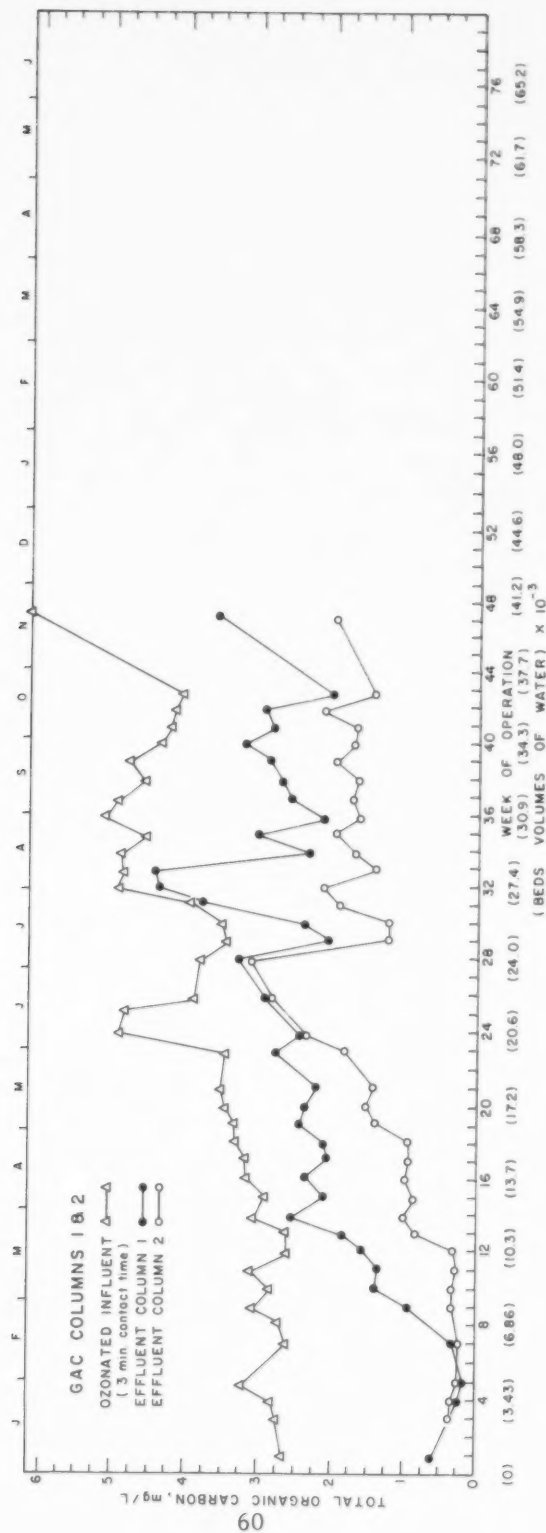


Figure 22. Total Organic Carbon Values for Short Contact Time Ozone Treated Water and Effluents of GAC Column Set.

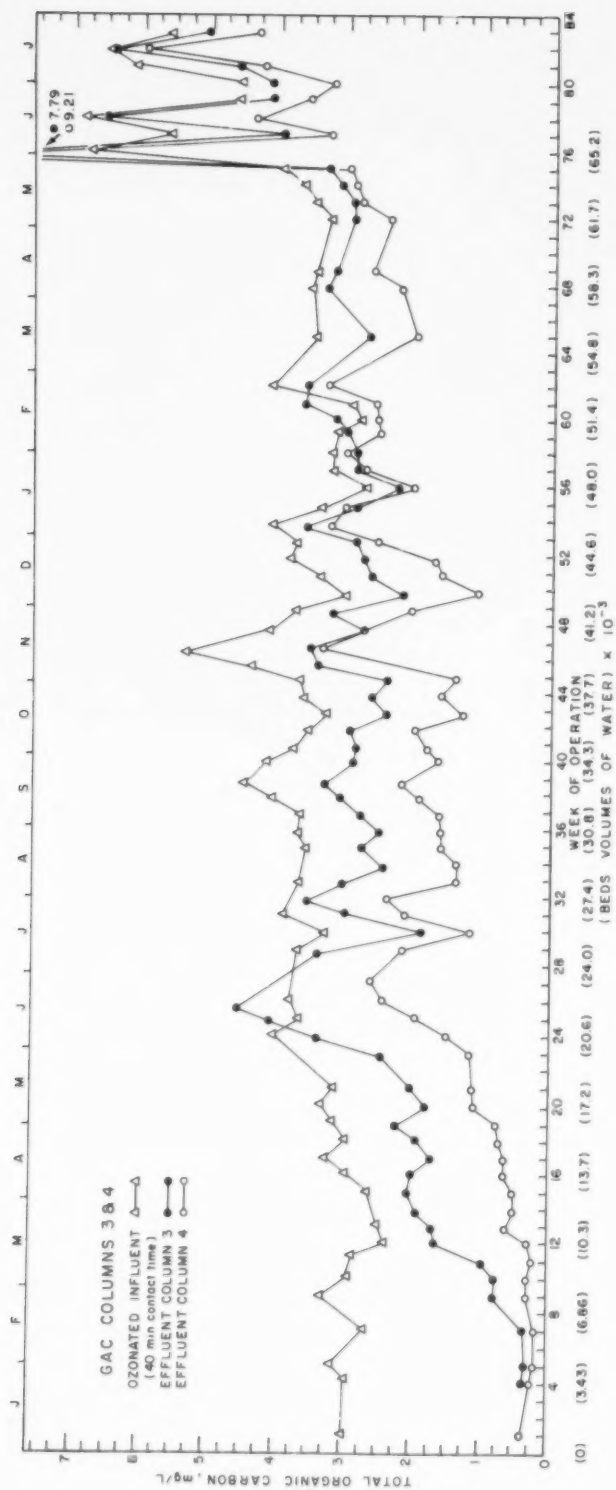


Figure 23. Total Organic Carbon Values for Long Contact Time Ozone Treated Water and Effluents of GAC Column Set.

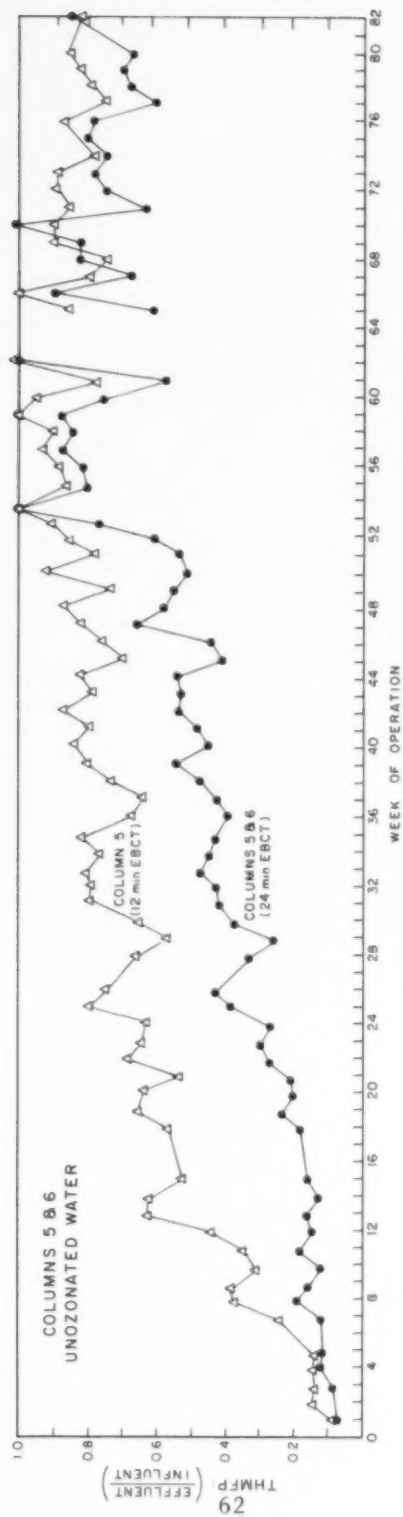


Figure 24. GAC Column Effluent/Influent THMFP Ratios for Settled-Filtered Water.

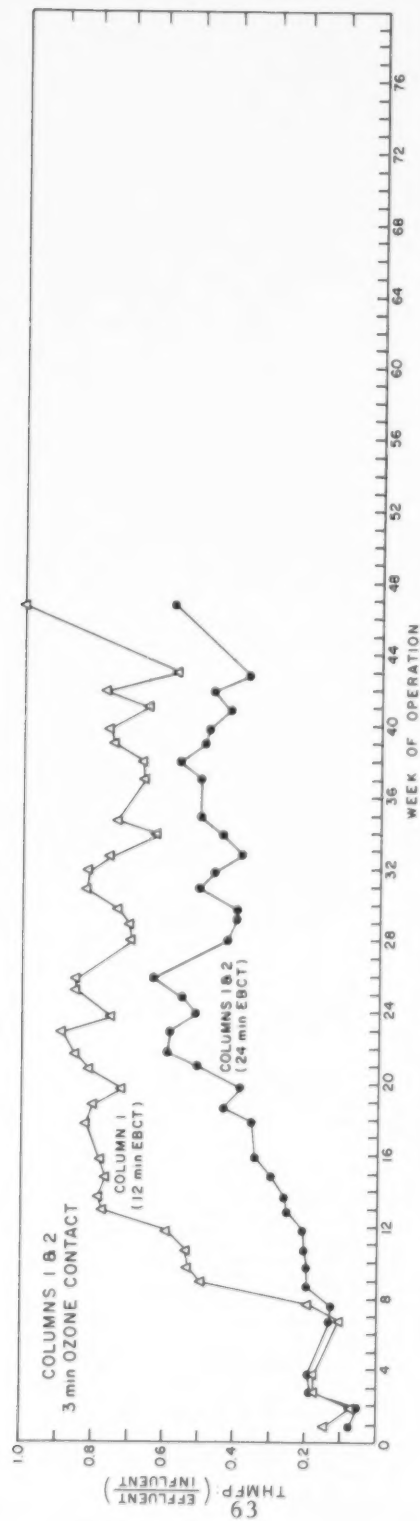


Figure 25. GAC Column Effluent/Influent THMFP Ratios for Short Contact Time Ozone Treated Water.

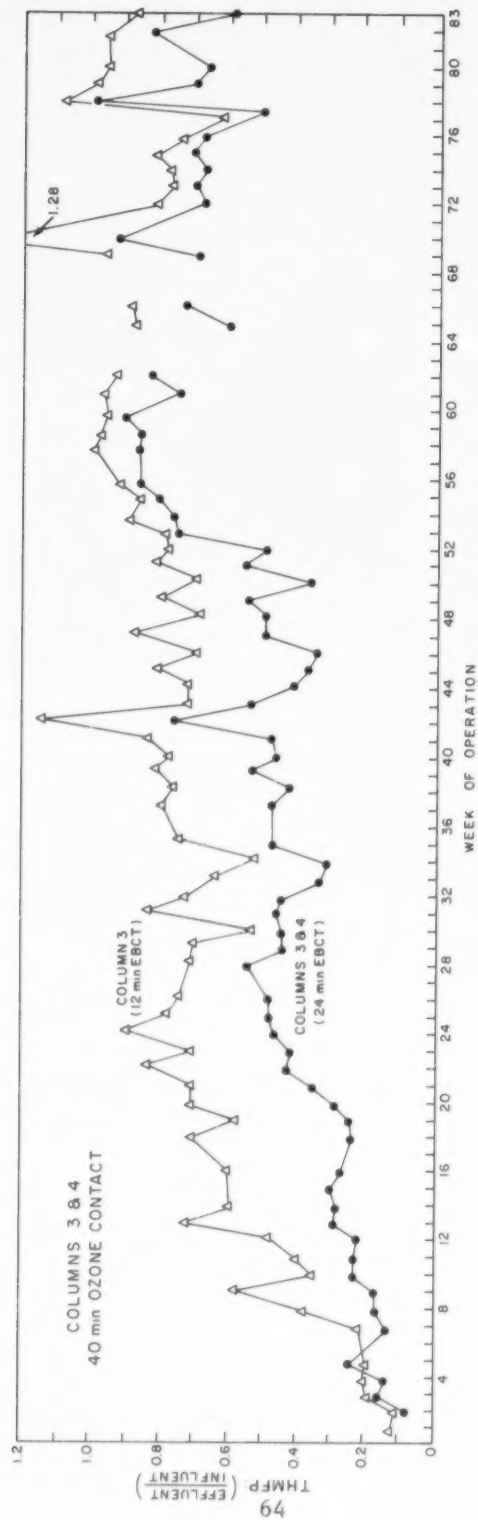


Figure 26. GAC Column Effluent/Influent THMFP Ratios for Long Contact Time Ozone Treated Water.

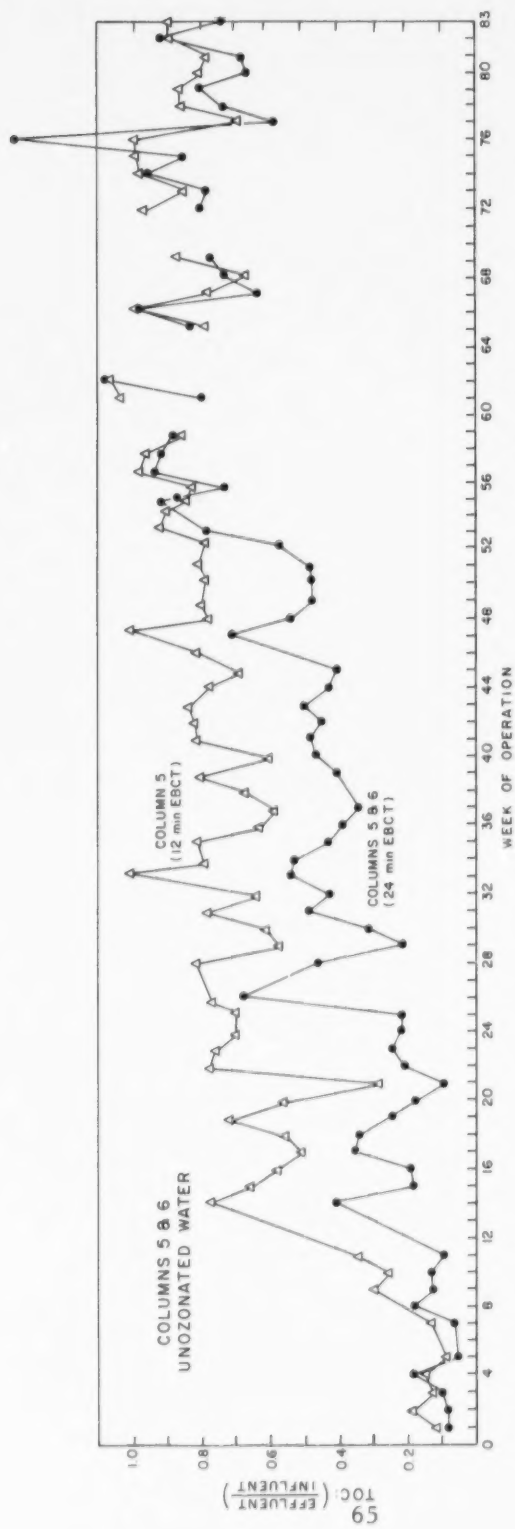


Figure 27. GAC Column Effluent/Influent TOC Ratios for Settled - Filtered Water.

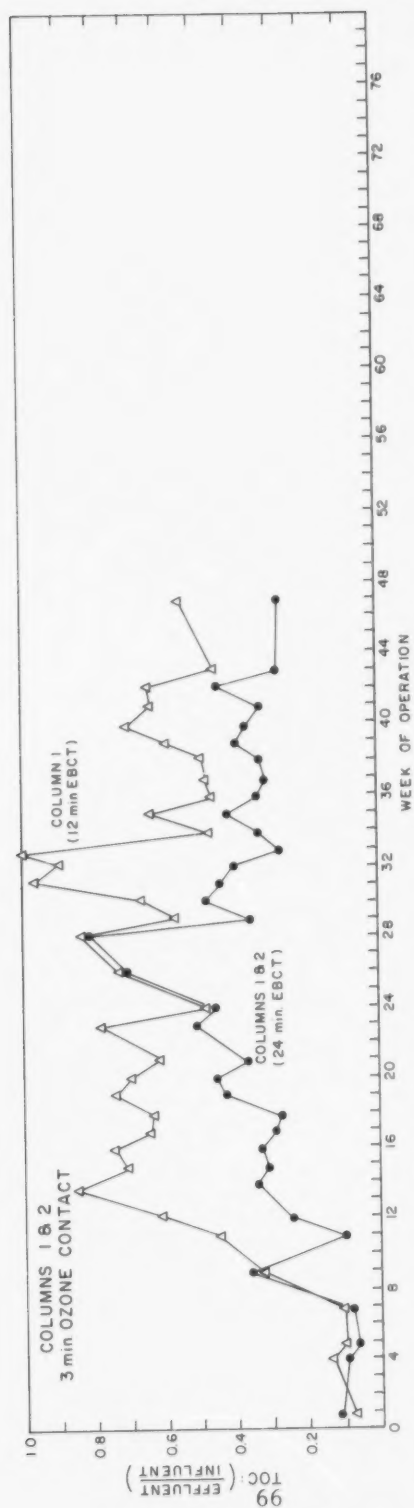


Figure 28. GAC Column Effluent/Influent TOC Ratios for Short Contact Time Ozone Treated Water.

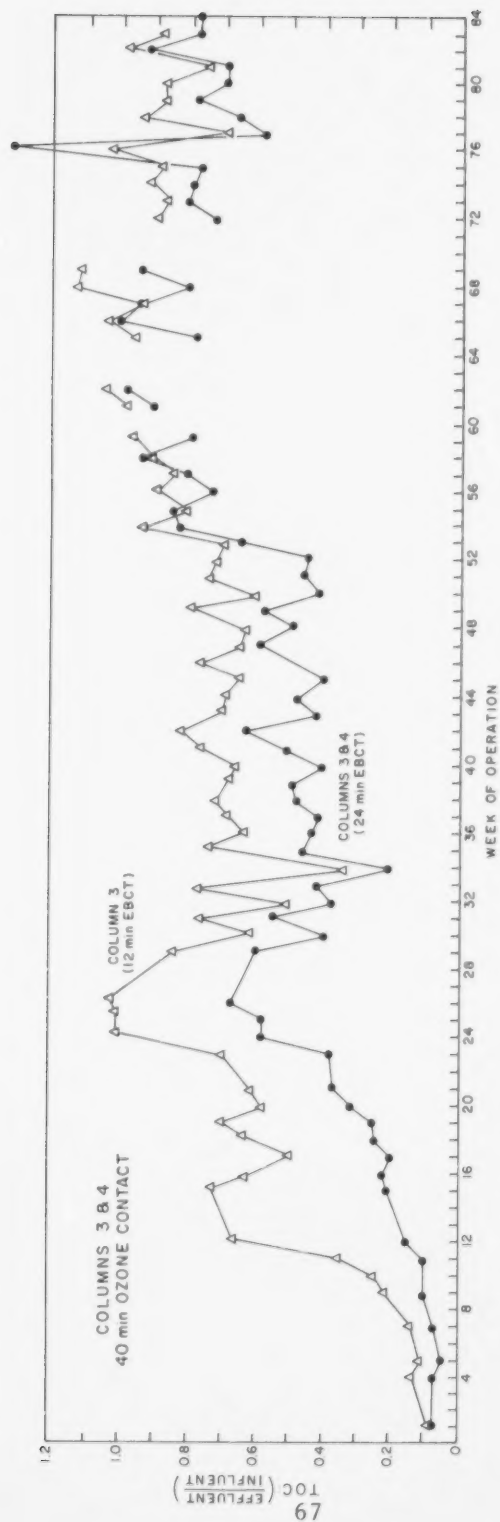


Figure 29. GAC Column Effluent/Influent TOC Ratios for Long Contact Time Ozone Treated Water.

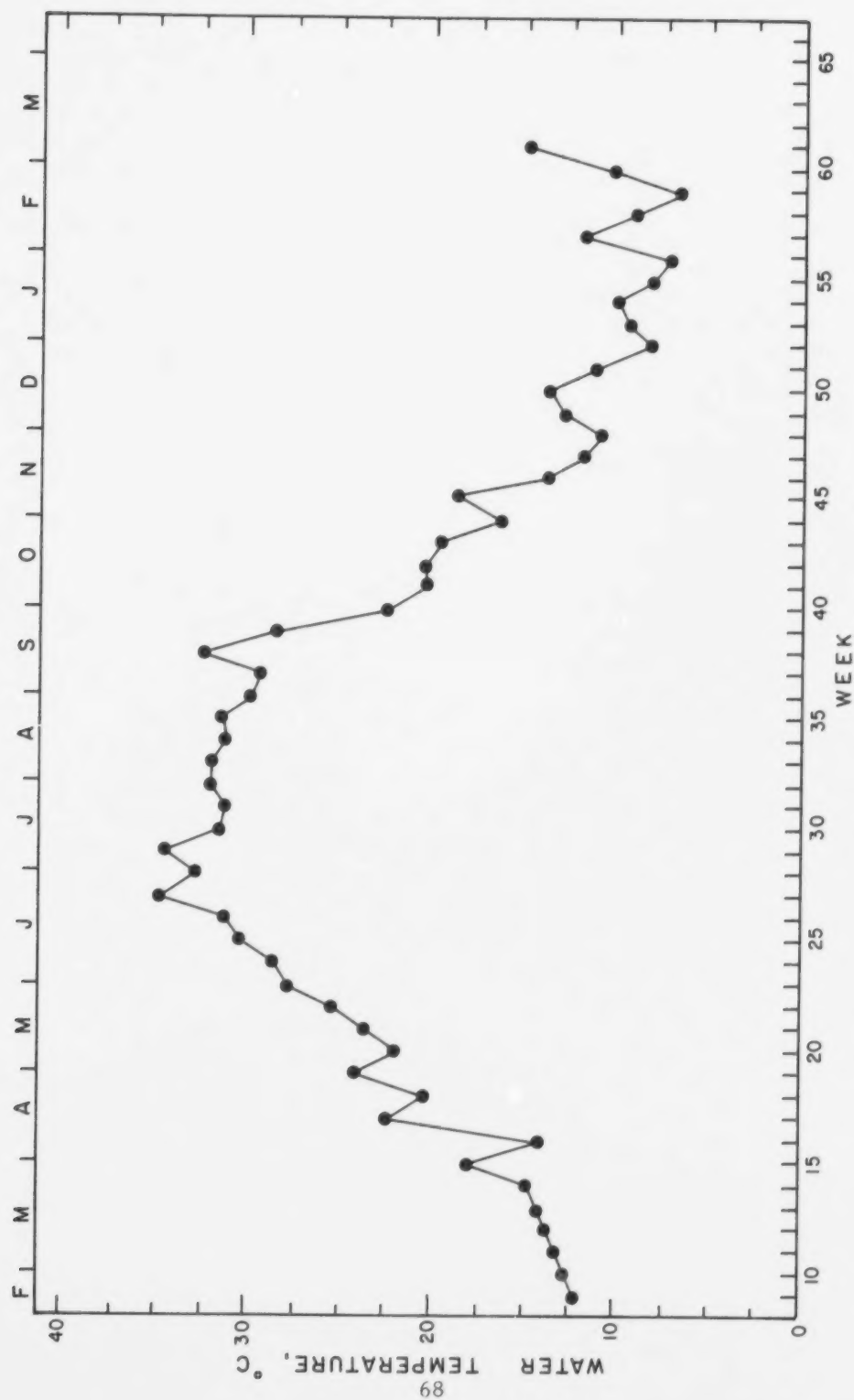


Figure 30. Annual Range of Water Temperature in the Pilot Plant Raw Water.

is not known what effect the downtime of these filters had on microbiological communities in the columns. Water was flowing through the columns most of the time, but it is possible that some diminution of the bacterial populations occurred. However, as shown in Figures 18-29 these columns appeared to resume at week 65 where they left off at week 63. Indeed, there was improved removal in this period as compared to weeks 52-63, the winter period. Removal rates of the column sets 5-6 and 3-4 during the last seventeen weeks of the project averaged approximately 25% of both TOC and THMFP.

Inorganic Carbon Production--

Values of dissolved carbon dioxide in its various forms were measured with the Dohrmann DC-54 analyzer and reported as total inorganic carbon (INC). Figures 31-32 show the increase in INC values across carbon column sets 5-6 and 3-4 respectively, expressed as mg CO₂/L. It is apparent from these plots that INC production is significant across GAC columns, and most importantly it is a function of the season. INC production is extremely low during winter months and high during warmer periods. Moreover, resumption of INC production occurred after the pilot plant was restarted at week 65 and rose to levels comparable to those observed the previous summer. A more quantitative discussion of this subject will follow in later parts of this section.

Microbiological Parameters--

Modified total plate counts (MTPC) and ATP values were determined on a biweekly basis on water taken at sample points 5, 7, 9, 11, 12 and 14; that is, before and after column sets 5-6, 1-2 and 3-4 respectively. Table 5 shows MTPC values obtained from this survey, and Figure 33 shows ATP and MTPC values for the life of the pilot plant. As shown in Table 5, water immediately after ozonation is very low in plate counts as compared to undisinfected water. One might conclude on this basis that microbial populations in the "ozonated" GAC columns would be proportionately lower than "non-ozonated" columns. However, as shown in Table 5, the effluent waters from columns 2 and 4 are by no means sterile; clearly these columns are functioning as "factories" for bacteria. The apparent net result is that both ozonated and non-ozonated GAC columns become heavily populated with bacteria during the first few months of operation. This process would undoubtedly have been accelerated by a start-up during the summer months, or by using undisinfected water for all columns, but the eventual result is the same.

Table 6 shows the results of measurements of modified total plate counts obtained from GAC and interstitial water samples taken directly from the columns. In addition Table 6 also lists dominant genera found by the selective culture techniques diagrammed in Figure 12. After July of 1980 ATP analyses were also conducted on samples from the GAC columns. These data are plotted in Figure 34 and listed in Table 7 where they are compared with total plate counts taken in part from Table 6. It is clear from these Tables and Figure 33 there are no gross differences in the levels of bacterial biomass in the ozonated vs. the unozonated GAC columns. Table 6 does show an apparently significant difference between CFU values in the first and second columns of a given set; i.e. bacterial counts

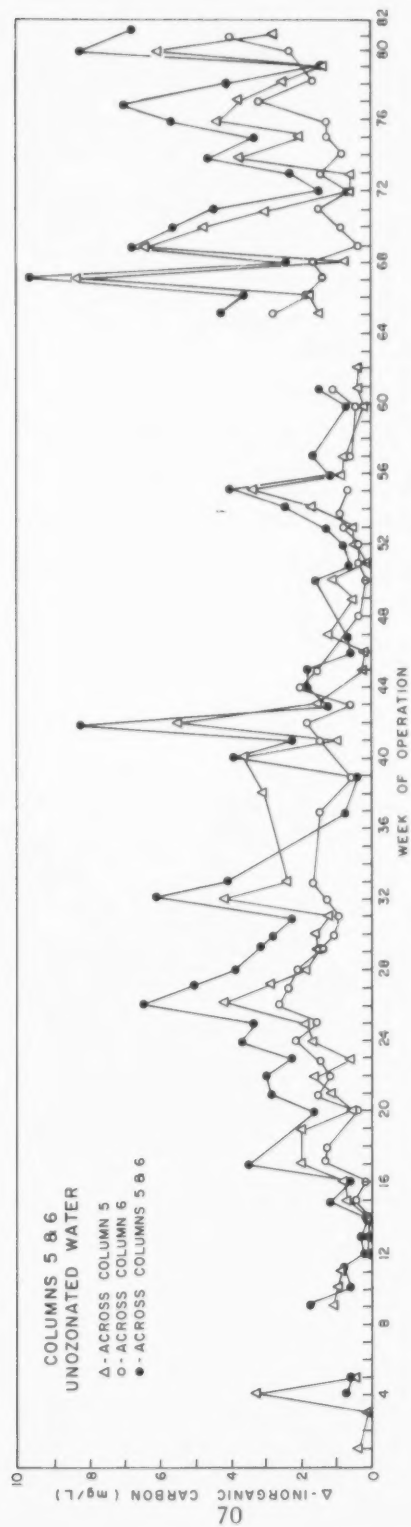


Figure 31. Difference in Inorganic Carbon Concentration of Settled - Filtered Water After GAC Filtration.

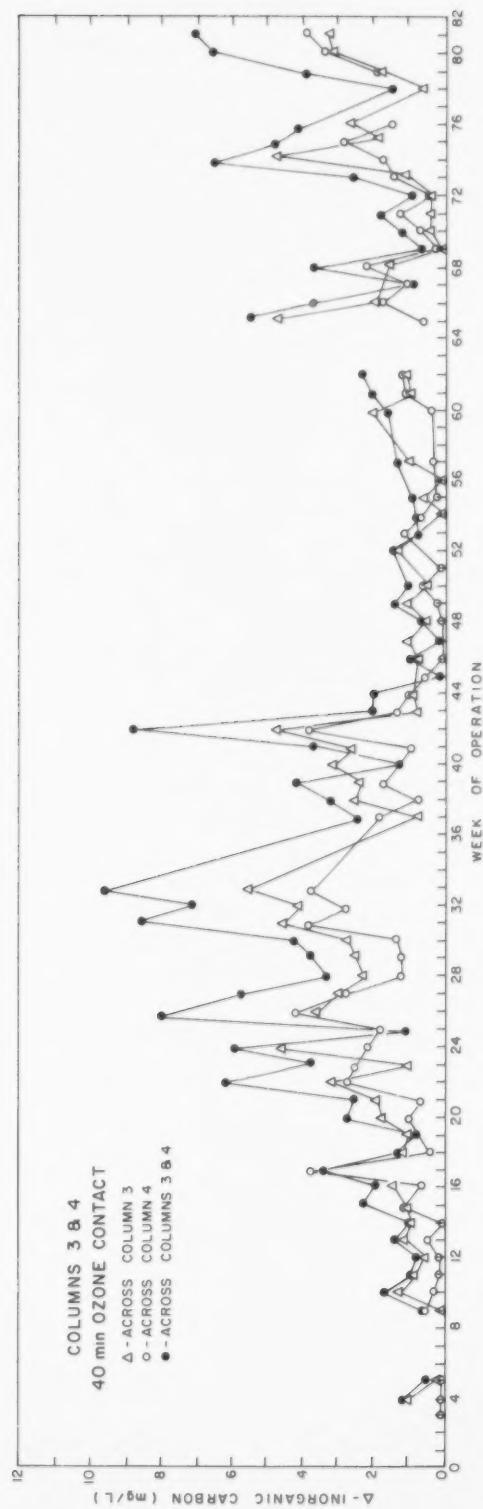


Figure 32. Difference in Inorganic Carbon Concentration of Long Contact Time Ozone Treated Water After GAC Filtration.

TABLE 5. MODIFIED TOTAL PLATE COUNTS (NG. mL⁻¹) OF INFLUENT AND EFFLUENT WATERS AS APPLIED TO SETS OF COLUMNS UNDER # & 25-40 MINUTE AND NO-O₃ CONTACT TIMES DURING THE 1ST OPERATIONAL PHASE OF THE BAC PILOT PLANT

DATE	3 min. contact-O ₃		25-40 min. contact-O ₃		No O ₃ Treatment	
	Before Column 1	After Column 2	Before Column 3	After Column 4	Before Column 5	After Column 6
1-4-80	0	717	0	494	1,527	1,066
1-23	0	1,877	0	1,465	2,790	3,720
2-12	2	188	5	90	145	150
2-26	5	480	8	15,000	2,600	2,300
3-26	0	10,000	0	3,500	10,000	5,000
5-6	0	1,630	150	2,350	6,050	3,050
6-3	1	2,000	336	4,610	1,200	5,150
7-8	300	15,000	290	13,000	3,315	4,100
8-12	0	300	30	1,100	2,500	550
9-15	1	680	78	3,400	400	1,600
10-6	16	1,300	9	550	130	750
11-12	25	300	240	1,500	1,700	300
12-8	*	*	2	1,275	1,920	7,550
1-13-81	*	*	3	3,560	82	67
2-10	*	*	5	1,700	110	70
3-24	*	*	55	2,900	660	150
4-15	*	*	226	2,200	165	240
5-14	*	*	202	4,650	300	130
6-16	*	*	870	2,910	550	140
7-16	*	*	2,876	2,386	700	155

*Biological and chemical monitoring of these columns ceased as of 12-1-80.

TABLE 6. BACTERIAL COLONY COUNTS USING THE MODIFIED TOTAL PLATE COUNT
TECHNIQUE AND DOMINANT GENERA FOUND IN GAC COLUMNS DURING
FEBRUARY-OCTOBER, 1980.

Date	Column No.**	CFU x 10 ⁻⁶		Dominant Genera*	
		per mL of interstitial water	per g dry wt. carbon ^a	interstitial water	carbon
2/1/80	1	0.01	0.08	NA	NA
	3	0.01	0.43	NA	NA
	5	0.01	NA	NA	NA
3/4	1	0.01	NA	NA	NA
	3	0.02	.11	NA	NA
	5	0.01	0.01	NA	NA
4/4	1	0.01	0.01	NA	NA
	3	0.02	NA	NA	NA
	5	0.01	0.07	NA	NA
5/7	1	0.02	2.00	NA	NA
	3	0.10	2.30	NA	NA
	5	0.01	1.50	NA	NA
6/13	1	0.11	2.0	12	1,2,4,13
	3	1.80	6.6	2,9,13	12
	5	0.04	2.0	12	2,6,9
7/10	1	0.50	12.0	11,12	2,9
	3	4.3	14.0	13	12
	5	1.80	36.0	13	12
8/1	1	4.0	20.0	6,11,12	11,12,13
	2	0.65	4.3	6,12	2,6,12,13
	3	6.0	8.0	6,12	2,6,12
	4	0.6	2.0	6,12	5,12,13
	5	0.76	1.6	3,6,7,9,12	3,6,7
	6	0.3	2.0	9,12	12
8/15	1	6.2	40.0	11,12	9,12
	2	1.6	18.0	12	9,12
	3	10.0	20.0	5,12	12
	4	0.5	11.0	12	12
	5	1.4	15.0	7,9,12	7,12
	6	0.77	33.0	7,12	7,12

TABLE 6 (continued)

Date	Column No.**	CFU x 10 ⁻⁶		Dominant Genera*	
		per mL of interstitial water	per g dry wt. carbon ^a	interstitial water	carbon
8/29/80	1	18.0	60.0	6,8,11,12	6,8,11,12
	2	3.7	10.0	4,6,8,12	6,8,12
	3	8.0	23.0	8,11,12	6,8,12
	4	1.8	8.0	6,13	6,8
	5	0.3	2.0	8,12	6,8
	6	2.0	2.6	6,8	8,12
9/12	1	1.2	23.0	12,13	1,12,13
	2	0.82	15.0	12,13	6,12,13
	3	0.4	33.0	4,6,12	4,6,12
	4	0.4	4.7	12,13	12,13
	5	0.18	2.0	10,12,13	9,12
	6	0.1	2.6	12,13	10,12
10/1	1	1.3	4.5	6,13	6,12,13
	2	0.9	6.6	4,6,12	6,12
	3	0.35	5.5	4,6,12	4,6,12
	4	0.6	0.5	2,6,13	6,12
	5	0.7	0.9	6,12	6,12,13
	6	0.25	2.7	2,6	6,13
10/27	1	1.0	2.7	6,13	6,12,13
	2	0.31	0.7	4,6,12	6,12
	3	0.65	1.4	4,6,12	4,6,12
	4	0.07	0.5	2,6,13	6,12
	5	0.05	0.3	6,12	6,12,13
	6	0.018	0.3	2,6	6,13
3/24/81	3	NA	46.0	NA	NA
	4	NA	35.0	NA	NA
	5	NA	56.0	NA	NA
	6	NA	58.0	NA	NA

(continued)

TABLE 6 (concluded)

Date	Column No.**	CFU x 10 ⁻⁶		Dominant Genera*	
		per mL of interstitial water	per g dry wt. carbon ^a	interstitial water	carbon
4/15/81	3	NA	496.0	NA	NA
	4	NA	68.2	NA	NA
	5	NA	242.1	NA	NA
	6	NA	95.0	NA	NA
5/14	3	NA	121.0	NA	NA
	4	NA	81.4	NA	NA
	5	NA	196.0	NA	NA
	6	NA	75.3	NA	NA
6/24	3	NA	135.0	NA	NA
	4	NA	92.0	NA	NA
	5	NA	250.0	NA	NA
	6	NA	144.0	NA	NA
7/16	3	NA	140.0	NA	NA
	4	NA	72.0	NA	NA
	5	NA	313.0	NA	NA
	6	NA	138.0	NA	NA

^a Counts per unit dry weight of carbon were obtained using a volume: curve (Figure 10) to convert counts/mL (packed volume of carbon) to counts/gr. dry wt.

*

Achromobacter (1), Acinetobacter (2), Aeromonas (3), Alcaligenes (4), Alcaligenes-like (5), Bacillus (6), Chromobacterium (7), Corynebacterium (8), Micrococcus (9), Microcylus (10), Paracoccus (11), Pseudomonas (12), Pseudomonas-like (13)

**

Column No. 1 receives water with an ozone contact time of 3 min.
 Column No. 3 receives water with an ozone contact time of 25-40 min.
 Column No. 5 received non-ozonated water.
 Columns No. 2 and 4 receive water from columns 1 and 3.
 Column No. 6 receives water from column 5.
 NA - Not Determined.

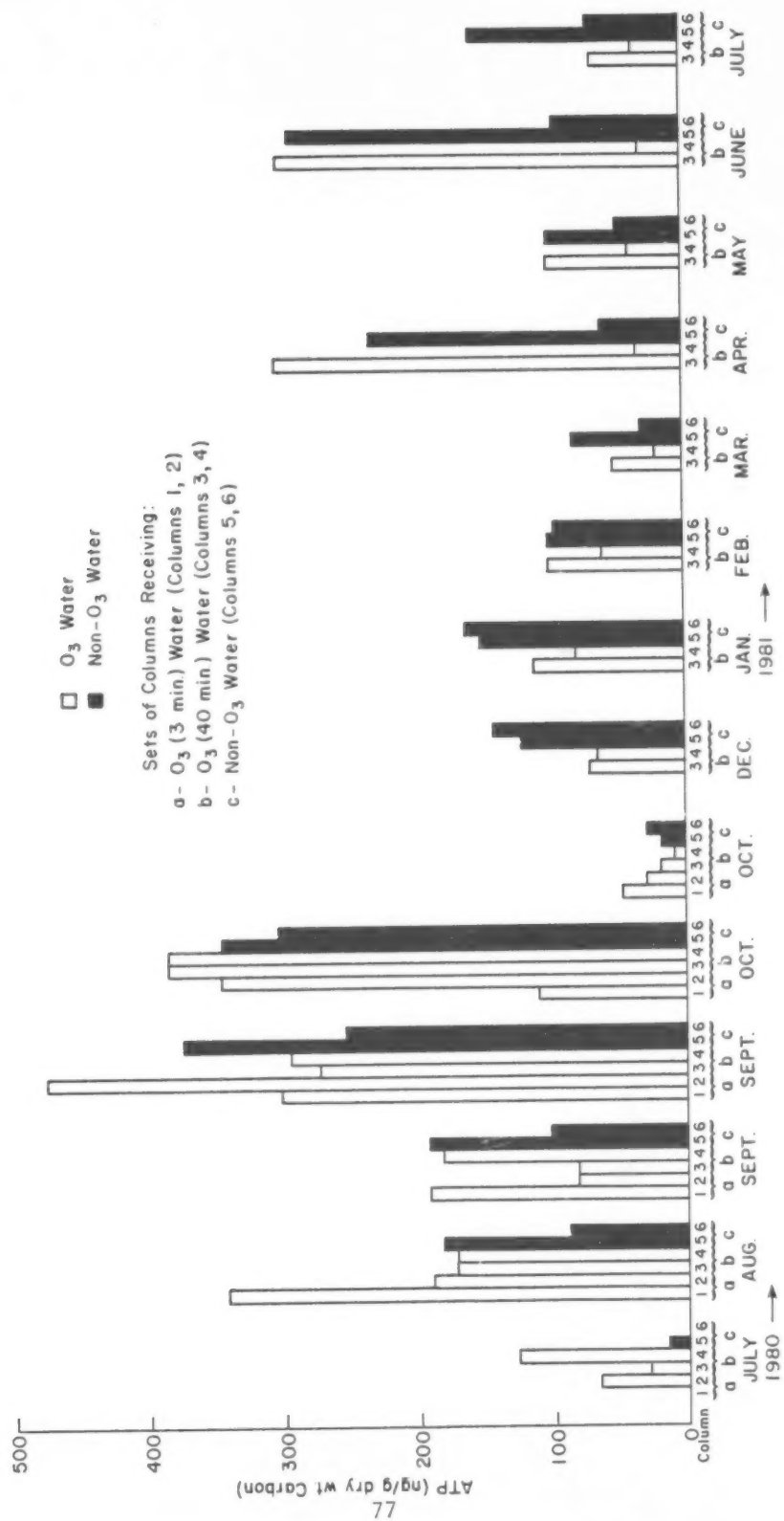


Figure 34. Microbial Biomass on GAC (using ATP) as Determined for Columns Receiving Ozonated and Non-Ozonated Water During July 1980 - July 1981

TABLE 7. ATP, MTPC, AND CORRELATION DATA ON GAC COLUMNS IN THE BAC
PILOT PLANT DURING THE PERIOD JULY 1980 - MAY 1981.†

Date	Column No.	ATP ng/g. dry wt. GAC	MTPC CFU x 10 ⁻⁶ per g. dry wt. GAC	Monthly Corr. Coef. a) r ²
7-10-80	1	*	12.0	*
	3	32.0	14.0	
	5	16.0	36.0	
8-26	1	342.0	60.0	0.90
	2	183.10	10.0	
	3	168.0	23.0	
	4	171.0	8.0	
	5	180.0	2.0	
	6	86.0	2.6	
9-12	1	185.0	23.0	-0.37
	2	72.0	15.0	
	3	79.0	33.0	
	4	179.0	4.7	
	5	189.0	2.0	
	6	98.0	2.6	
10-1	1	294.0	4.5	0.33
	2	474.0	6.6	
	3	266.0	5.5	
	4	286.0	0.5	
	5	377.0	0.9	
	6	255.0	2.7	
10-23	1	49.0	2.7	0.70
	2	31.0	0.7	
	3	18.0	1.4	
	4	10.0	0.5	
	5	18.0	0.3	
	6	30.0	0.3	
12-18	3	71.0	*	*
	4	65.0	*	
	5	120.0	*	
	6	127.0	*	
1-13-81	3	109.0	*	*
	4	76.0	*	
	5	125.0	*	
	6	142.0	*	

(continued)

TABLE 7 (concluded)

Date	Column No.	ATP ng/g. dry wt. GAC	MTPC CFU $\times 10^{-6}$ per g. dry wt. GAC	Monthly Corr. Coef. ^{a)} r^2
2-11-81	3	95.0	*	*
	4	61.0	*	
	5	68.0	*	
	6	93.0	*	
3-24	3	48.0	46.0	0.53
	4	19.0	35.0	
	5	79.0	56.0	
	6	29.0	58.0	
4-15	3	305.0	496.0	0.95
	4	30.0	68.0	
	5	227.0	242.1	
	6	58.0	95.0	
5-14	3	97.0	121.0	0.84
	4	36.0	81.4	
	5	100.0	196.0	
	6	45.0	75.3	
6-24	3	298.0	135.0	0.65
	4	34.0	92.0	
	5	286.0	250.0	
	6	88.0	144.0	
7-16	3	65.0	140.0	0.95
	4	34.0	72.0	
	5	157.0	313.0	
	6	69.0	138.0	

* no data generated

† ATP and MTPC sampling was discontinued on columns 1 and 2 after the October 1980 sampling period.

a) Correlation coefficients established via regression of monthly ATP/MTPC data.

predominate in the first of each two column series. This may be due to a filtering action in the first GAC column (54), but in addition it is also consistent with the tendency of most biological filters to utilize whatever biodegradable materials are present in the early stages of the filter (73). Further comments on this behavior are given in subsequent parts of this section.

Table 8 reveals the CFU's per gram dry weight of carbon as determined on five selective culture media. Analysis of these data for trends and relationships to "modified total plate counts" on SEA (Soil Extract Agar) are difficult. The majority of the organisms present in the GAC columns are Gram-negative as evidenced by the relatively high plate counts on McConkey agar, a medium generally selective for Gram-negative bacteria. Actinomycetes were found to exist in somewhat greater numbers during the later part of August than at other periods.

The inability of the Pseudomonas Isolation Agar (PIA) to support the growth of many bacteria more than likely is a result of the severe specificity of this medium attributable to the selective agent, "Irgasan" (halo-o-hydroxydiphenyl ether), present in an amount of 0.025 g/L. Thus, the Pseudomonas medium is generally toxic to most aquatic pseudomonads; it was not difficult to isolate Pseudomonas spp. from the higher dilutions of plates containing SEA. Further evidence of the toxicity of PIA was obtained by comparing drop plate counts of nutrient broth cultures of three stock species of pseudomonads on PIA and on nutrient agar. Actually, no growth appeared on PIA plates seeded with dilutions of young broth cultures of P. aeruginosa and P. stutzeri. The colony count of P. fluorescens on the PIA plates was $8.5 \times 10^3/\text{mL}$ while the same culture plated on nutrient agar revealed a plate count of $7.8 \times 10^4/\text{mL}$.

Fungi and nitrogen-fixing bacteria were found in modest numbers, generally $<10^3/\text{gram dry wt.}$). They were most abundant during the warmer months. Those carbon filter organisms that were isolated and identified according to the scheme shown in Figure 12 are displayed in Table 8. Since these represent isolates from the higher dilutions of the SEA plates, they constitute the most abundant genera. The dominant groups of these bacteria are Pseudomonas spp. and Bacillus spp. Other principal bacterial types include species of Chromobacterium, Alcaligenes, Acinetobacter and Micrococcus. It is not possible to relate the nature of the bacterial population on the carbon particles or in the interstitial waters to such variables as ozonation and season (temperature). Undoubtedly, genera of bacteria other than those identified were present in the samples tested; however, they were present in smaller numbers because pure culture isolations, of necessity, were made from the higher dilution plates in which the colonies were less crowded.

Organisms in the coliform group were not present in any of the influent and effluent waters associated with the GAC columns until July, 1980 when low numbers (1-4 organisms per 100 mL) were noticed in the effluents of columns 2, 4 and 6. The magnitude of these concentrations co-varied with seasonal changes throughout the rest of the study period (Table 9). Organisms in the fecal coliform group were never found in any of

TABLE 8. COLONY COUNTS OBTAINED FROM CARBON PARTICLES USING ORGANISM TYPE SPECIFIC MEDIA AND SONIFICATION METHODOLOGIES

Sample Date (1980)	Column No.	CFU x 10 ⁻² /Media Type (per gram dry wt. GAC)				
		McConkey	Actino. Isolation A	Pseudomonas Isolation A	Burkes	Cooke Rose Bengal Agar
6/13	1	9.0	5.0	0	2.5	1.0
	3	1200.0	2.0	0	0	1.0
	5	1500.0	1.2	0	0.3	0.1
7/10	1	90.0	40.0	1.0	47.0	2.0
	3	300.0	10.0	0.2	1.3	0.2
	5	400.0	2.0	0	4.0	0.1
8/1	1	40.0	4.0	0	1.0	0
	2	0.1	4.0	0	1.0	7.0
	3	1.0	2.0	0	0	0
	4	18.0	4.0	0	0.2	0
	5	35.0	0.6	0	0	0
	6	19.0	4.0	0	0	0.5
8/15	1	3.0	6.0	0	10.0	1.0
	2	4.0	7.6	0	3.0	2.0
	3	13.0	4.0	0	0	0.5
	4	12.0	26.0	0	0	0.8
	5	35.0	14.0	0	0	0.2
	6	60.0	40.0	0	1.0	3.0
8/29	1	9.0	12.0	0	0	.2
	2	3.5	44.0	0	0	1.0
	3	4.0	10.0	0	0	2.0
	4	11.0	1.2	0	0	0
	5	4.0	10.0	0	0	0.2
	6	2.0	6.0	0	0	0.5
9/12	1	5.0	10.0	0	0	4.0
	2	10.0	7.5	0	0	0
	3	1.2	0.5	0	0	0
	4	13.0	0.2	0	0	2.0
	5	3.0	2.0	0	0	0.5
	6	1.1	1.2	0	0	0

(continued)

TABLE 8. (concluded)

Sample Date (1980)	Column No.	CFU x 10 ⁻² /Media Type (per gram dry wt. GAC)				
		McConkey	Actino. Isolation A	Pseudomonas Isolation A	Burkes	Cooke Rose Bengal Agar
10/1	1	2.0	10.0	0	0	0
	2	22.0	3.2	0	0	0
	3	17.0	6.0	0	0	0
	4	20.0	2.2	0	0	0
	5	1.4	10.0	0	0	0
	6	3.0	48.0	0	0	0
10/27	1	20.0	4.0	0	0	1.0
	2	50.0	1.2	0	0	0
	3	42.0	0	0	0	0
	4	40.0	0	0	0	0
	5	10.0	1.4	0	0	0
	6	10.0	2.4	0	0	0.3

* Microbial Groups responsive to media types:

- McConkey Medium-Gram (-) bacteria: A select few *Pseudomonas* species and most *Enterobacteriaceae* species.
- Actinomycete Isolation A - Actinomycete organisms.
- Pseudomonas* Isolation A - *Pseudomonas* groups of organisms:
P. fluorescens mainly.
- Burkes Medium-Nitrogen fixing bacteria: *Azotobacter* sp.
- Cooke Rose Bengal Agar - Most types of fungi.

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TABLE 9. TOTAL AND FECAL COLIFORM DENSITIES (NO/100 mL) IN INFLUENT
AND EFFLUENT WATERS OF THE GAC COLUMNS IN THE PILOT WATER
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Date	Sta. No.	Total Coliform #/100 mL	Fecal Coliform #/100 mL
1/23/80	5,6,7,9,10 11,12,13,14	0	0
2/12	5,6,7,9,10 11,12,13,14	0	0
2/26	5,6,7,9,10 11,12,13,14	0	0
3/26	5,6,7,9,10 11,12,13,14	0	0
5/6	5,6,7,9,10 11,12,13,14	0	0
6/2	5,6,7,9,10 11,12,13,14	0	0
7/8	5,6,9,10,12,13 7 11 14	0 4 2 1	0 0 0 0
8/12	5 6,9,10,11,12, 13,14 7	1 0 8	0 0 0
9/15	5 6 7 9 10 11,13 12 14	9 8 7 0 4 3 1 2	0 0 0 0 0 0 0 0

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Date	Sta. No.	Total Coliform #/100 mL	Fecal Coliform #/100 mL
10/6	5	4	0
	6,13,14	1	0
	7	2	0
	9,10,11,12	0	0
11/12	5	9	0
	6	4	0
	7,13	1	0
	9	2	0
	10,12	5	0
	11	3	0
	14	0	0
12/8	5,6,7	*	*
	9	6	0
	10	3	0
	11	1	0
	12,13,14	0	0
1/13/81	5,7	2	0
	6,12,13,14	0	0
2/10	5	4	0
	6	11	0
	7	5	0
	12	0	0
	13	6	0
	14	15	0
3/24	5,7,14	1	0
	6	*	*
	12	5	0
	13	**	**
4/15	5	0	0
	6,13	**	**
	7	1	0
	12	7	0

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TABLE 9. (concluded)

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Date	Sta. No.	Total Coliform #/100 mL	Fecal Coliform #/100 mL
5/14	5	8	0
	6,13	**	**
	7	7	0
	12	1	0
	14	28	0
6/24	5	33	0
	6,13	**	**
	7	455	0
	12	135	0
	14	80	0
7/16	5	25	0
	6,13	**	**
	7	215	0
	12	81	0
	14	91	0

* These sampling points were removed from the monthly sampling regime for conversion to other activities in Phase I-E-2 of the project. They are not listed in this table after December.

** During these months these stations were not monitored for coliform organisms.

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the influent and effluent waters. It should be noted that total and fecal coliform organisms were found in relatively high numbers, $10^2 - 10^4$ and $10^1 - 10^2$ organisms per 100 mL respectively, in raw lake water coming to the pilot plant facility during the study period.

Results Obtained from Phase I-E-2: GAC Columns 9, 10, 11 and 12

The second pilot scale phase consisted of careful studies of the chemical and biological behavior of four new columns. The new flow pattern is diagrammed in Figure 9 and the new columns are listed here again for convenience of the reader.

TABLE 10. DESCRIPTION OF THE NEW COLUMNS OPERATED IN PHASE I-E-2.

Column No.	Influent Water		Medium	Sample Point	
	Ozonated	GPM		Before	After
9	Yes	2	Sand	12	16
10	No	2	Sand	5	18
11	Yes	2	GAC	12	15
12	No	2	GAC	5	17

The impetus for the studies during this phase of the project was threefold:

1. To provide additional biomass data during the early phase of GAC column operation.
2. To ascertain any differences in microbial growth between sand and GAC substrates for eventual comparisons to total organic carbon removal efficiencies for these two substrate types.
3. To provide additional chemical data in order to model more accurately the adsorption and microbiological removal processes which occur in the GAC columns.

Samples of sand and GAC were taken from the columns for ATP and MTPC determinations, the former on a weekly and the latter on a bi-weekly basis. Samples shipped (on ice) via express bus to NTSU for analysis were composite samples obtained by taking equal or near equal carbon (GAC) or sand samples from the top and middle sampling ports of each column.

Procedures for determining MTPC and ATP concentration on the new carbon and sand columns (numbers 9, 10, 11 and 12) were almost identical to methods used in Phase I-E-1 with the exception that the samples were composited as noted above. Chemical measurements were determined on the

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influent and effluent waters to each GAC column using the methodologies described earlier in this report.

Figures 35 and 36 show the values of ATP and MTPC obtained during the seventeen week Phase I-E-2 study. Modified total plate count data indicate that substantial microbial growth occurred on both the sand and GAC substrates during the phase I-E-2 study period (figure 36). However, MTPC values were approximately one order of magnitude lower than MTPC values observed during the same period in columns 5 and 3 (Table 7). Microbial populations were initially greater on the sand particles than on the GAC; a trend that tended to reverse itself during June and July. On a temporal basis fluctuations of MTPC and ATP concentration compared favorably. Weekly measurements of ATP (see figure 35) indicated that generally the differences between sand and GAC microbial biomass were not great except during the first few weeks. It is interesting to note that the ATP concentrations on GAC did not fluctuate as widely as those ATP concentrations on sand particles.

Ozonation does not appear to significantly enhance microbial growth on either the GAC or sand. As noted before, microbial growth tends to establish itself more readily on those substrates receiving non-ozonated water than those receiving ozonated water; but the difference is minimal after a period of one month to six weeks.

Chemical data obtained during Phase I-E-2 will be presented in more detail in a later part of this section. However, one parameter was added in this phase which was not measured in Phase I-E-1, i.e. non-purgeable total organic halogen (NPTOX) formation potential. This parameter was measured for columns 11 and 12 which were started at the beginning of Phase I-E-2. A limited amount of data was obtained from samples taken at other sites in the plant; the data is tabulated in Table 11.

The NPTOX method used is an adaptation of the original GAC method of Kühn and Sontheimer (74) and modified by Takahashi et al. at Dohrmann Envirotech (75). Samples were treated exactly as they would be for determination of THMFP. Instead of LLE extraction after chlorination, however, the sample (25 mL) was purged for approximately 15 minutes with helium gas to remove all volatiles. Analysis of one of the purged samples showed no remaining THM's after this period. Using the TOX-1 Module, the sample was passed through a glass tube containing 40 mg of crushed 80/100 mesh Filtrasorb-400 obtained from R. Dressman (USEPA/MERL Cincinnati). The GAC was washed with nitrate and combusted according to the Dohrmann procedure (75). A Dohrmann Model MCTS-20 microcoulometer titration system with single boat accessory was used. Data are reported as $\mu\text{g Cl/L}$ of sample. Figures 37 and 38 show plots of NPTOX for columns 11 and 12 for the period of study.

Unfortunately the NPTOX method used here is slow and tedious, and only a limited number of samples could be run before the project terminated. More modern equipment is now available to reduce the time required for the analysis, but it was unavailable for this project.

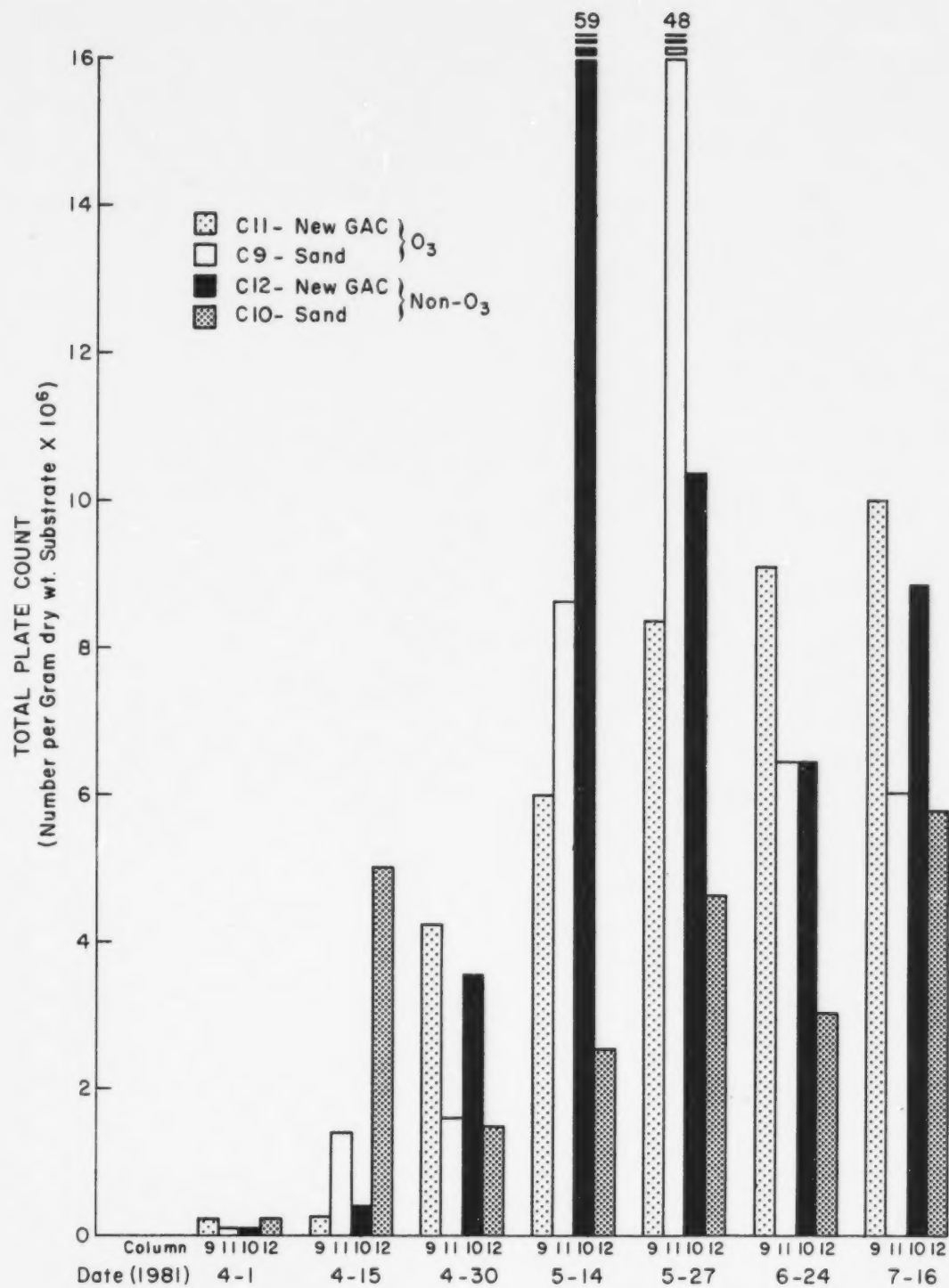


Figure 36. Microbial Biomass on Sand and GAC Columns as Measured by Modified Total Plate Counts on Soil Extract Agar in Phase I-E-2.

TABLE 11. NON-PURGEABLE ORGANIC HALOGEN LEVELS IN THE PILOT PLANT
AT SHREVEPORT, LA.: PHASE I-E-2

WEEK	DATE	NPTOX ($\mu\text{g Cl/L}$) at SITE NO.										
		1	5	6	7	12	13	14	15	16	17	18
71 (5)	5-5-81		347			270			90		192	
72	5-12		323			328			97		113	
73	5-19		462			395			109		186	
74	5-26		378			325			65		145	
75	6-2					391			152		130	
76	6-9		398			396			88			
77	6-16		512			512			71		128	
78	6-23		1403			1174					352	
79	6-30		818			558		479	178		1038	
80	7-7	1562	903	525	480	758	339	845	197	354	240	492
81	7-14											
82	7-21	1300	874	863	786	718	658	600	300	711	494	854
83(17)	7-28	1811	1226	759	650	1138	882	517	533	855	516	845

Site description: 1(raw water); 5(settled-filtered water); 5-6-7(sample points on GAC columns 5&6); 12(after ozone contacting and detention, 3.4 mg/L dose); 12-13-14(sample points on GAC columns 3 & 4); 5-17(sample points before and after GAC column 12, unozonated); 5-18(sample points before and after sand column 10, unozonated); 12-15(sample points before and after GAC column 11, ozone treated); 12-16(sample points before and after sand column 9, ozone treated).

Week number in parenthesis refers to time elapsed after Phase I-E-2 began and new columns were on-line.

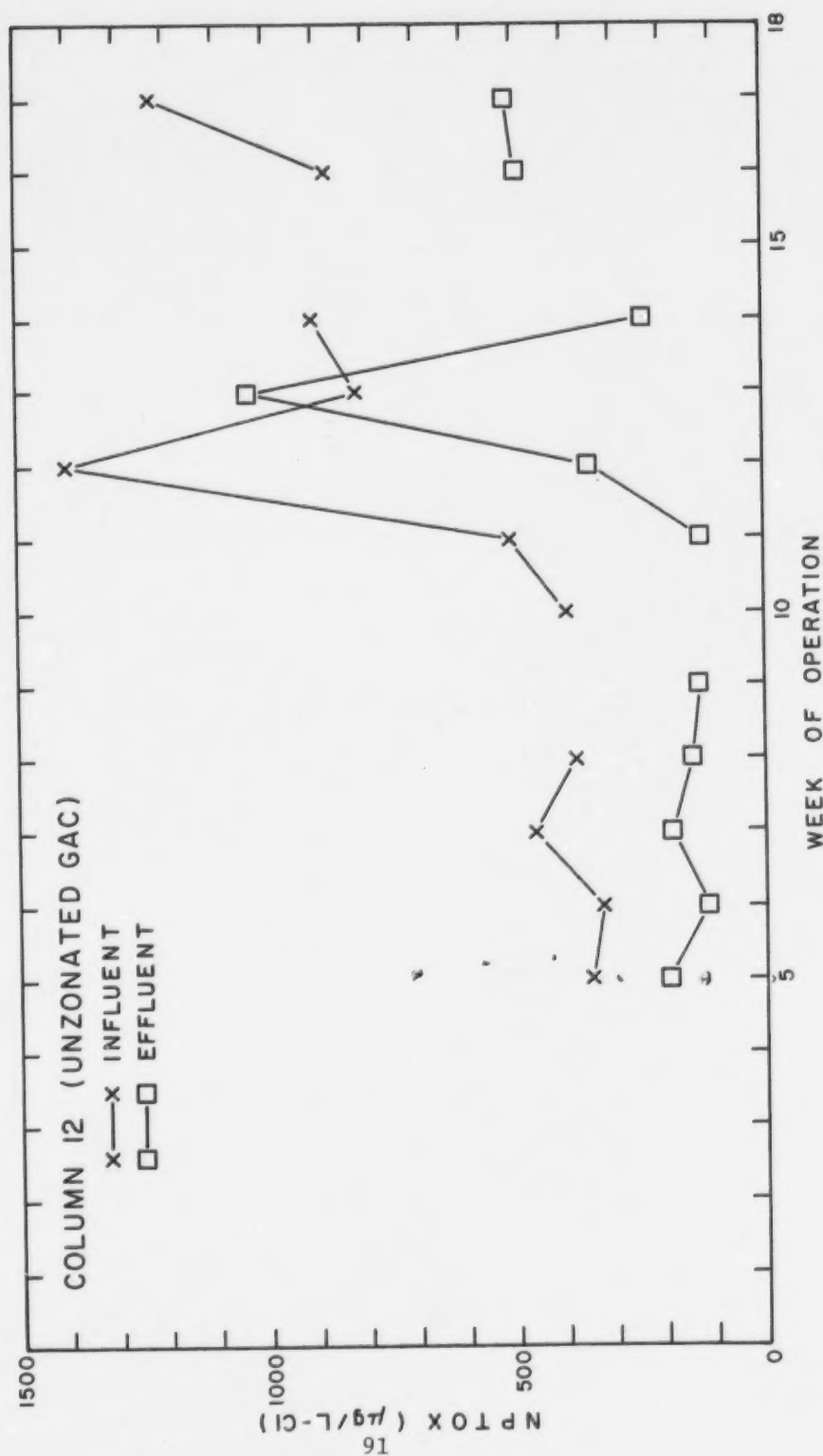


Figure 37. Nonpurgeable Organic Halogen Formation Potential of Settled - Filtered Water Before and After GAC Column 12, Phase I-E-2.

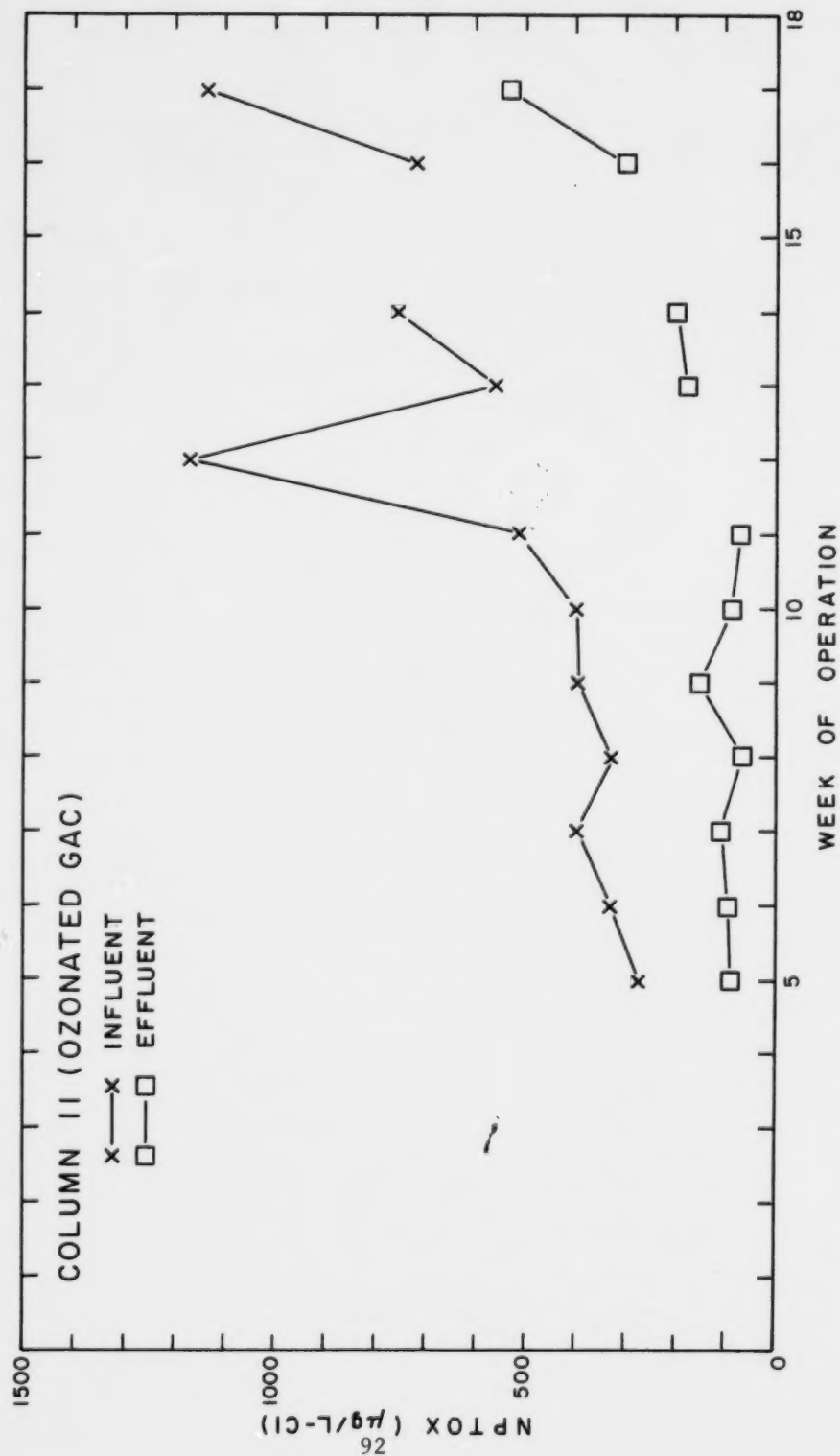


Figure 38. Nonpurgeable Organic Halogen Formation Potential of Ozonated Water Before and After GAC Column 11, Phase I-E-2.

DISCUSSION

Discussion and Conclusions from the Microbiological Data

When interpreting the microbiological data generated during the operational phase of the pilot plant it should be noted that while the absolute values presented for each parameter are important, it is actually the trends and comparative analysis between and among parameters that contribute to the overall understanding of the treatment process. An example of this would be the values and comparison of ATP and MTPC generated for the influent and effluent waters to and from the GAC columns and on the GAC itself (Table 7). ATP values for instance, represent the instantaneous amount of viable micro-organisms present in the sample medium at the time of extraction. However, any time the sample medium changes or the environment changes in which the organisms are growing, shifts in the adenylate charge (i.e. concentration of cellular ATP) of each cell may occur; in fact it usually does occur as noted in other studies on aquatic micro-organisms by Wiebe and Bancroft (76) and Chapman *et al.* (77). It is possible then that when extracting ATP lower or higher values of ATP may be obtained should shifts in a cell's adenylate charge ratio occur at the time of extraction. The authors above however, have noted that although shifts in adenylate charge occur very rapidly, they rarely remain at the changed levels; all of which is a function of how long it takes the organisms to adjust to their environmental change. ATP concentrations may also be influenced either positively or negatively by extraction mediums, operator error, and/or bacterial contamination of frozen extracts. Absolute values of modified total plate counts must also be viewed with caution since not all organisms present in the GAC columns will grow on soil extract agar (SEA) even though the efforts of McElhaney (67) and others have shown that a greater diversity of organisms grow on SEA than any other medium currently in use, at least for GAC related studies. Bearing in mind then the pitfalls of the ATP and MTPC assays, it was not surprising that yearly comparisons between ATP and MTPC concentrations on GAC for each column correlated very poorly ($r^2 = .13$). However, when ATP and MTPC concentrations on GAC for all columns were regressed on a monthly basis, correlation coefficients (r^2) proved to be much higher (0.3 to 0.95). One exception was during the month of September 1980 where the r^2 value = -0.37. We are not sure why concentrations of ATP and MTPC did not fluctuate together during this period. These correlations confirm that as growth monitoring parameters ATP and MTPC tend to reflect similar responses in microbial shifts that occur on GAC. Similar findings were obtained by McElhaney, *et al.* (78) using total plate count methods to monitor microbial population shifts on GAC columns.

The effect of ozonation (as a pretreatment process) on microbial metabolism of organic material has been studied in varying degrees by several authors [Guirguis *et al.* (79) Weber *et al.* (80), and Van der Kooij (81, 82)]. Most of these authors have found that preozonation of GAC influent waters tend to enhance microbial growth on GAC particles, but as noted earlier this is not a unanimous verdict. During the first half of this study Phase I-E-1, it was shown that this phenomenon appeared to be true, the second half of the study revealed that growth on the non-ozonated

columns was starting to exceed the growth on the ozonated columns, at least as indicated via measurements of ATP and MTPC. The cause of this shift is not yet clear. The fact that during this period the effluents of the ozonated columns were much higher in microbial numbers than the non-ozonated columns effluents suggests that perhaps the ozonated columns were operating in a sloughing mode whereas the non-ozonated columns were continuing in their normal operational mode. Another possibility is that the non-ozonated GAC columns were starting to act as filters for microbial organisms; a possible explanation for the generally lower numbers of organisms in the effluent waters as opposed to the higher numbers in the influent waters at this time.

The predominant microbial genera isolated during the study were saprophytic chemo-organotrophs of the gram positive/negative aerobic rod types (i.e. Pseudomonas and Bacillus spp.) all of which are common in aquatic and soil mediums. Many of these organisms have been found to decompose humic and fulvic acids [Burgess and Latter (83); Federov and Illna (84); Mathur (85); Mathur and Paul (86)] and were readily expected in our isolates. McElhaney et al. (87) and Werner et al. (88) have also found these types of organisms in similar studies involving GAC substrates.

The micro-organisms isolated from SEA or appearing on selective agars inoculated with BAC specimens are typical aquatic species with most belonging to the family Enterobacteriaceae. However, Pseudomonas, Alcaligenes, and some types of fungi were encountered that are known to be opportunistic pathogens. The presence of coliform organisms in GAC column effluents during the later stages of the study suggests that other pathenogenic organisms may be present in very low numbers.

In summary the biological studies associated with Phase I-E-1 of the pilot study indicate the following:

1. Modified total plate count and ATP data generated on influent and effluent waters and on the GAC itself indicate that substantial microbial growth does occur on GAC columns.
2. Correlation of ATP and MTPC data show that these two parameters generally respond in the same way to positive or negative shifts in microbial populations on GAC. Similar results are indicated in influent and effluent waters.
3. During the early stages of operation preozonation of influent waters appears to enhance microbial growth on GAC columns. On a cumulative basis however, microbial biomass data suggests that preozonation does not significantly enhance microbial growth on GAC.
4. Microbial concentrations on GAC and in the influent and effluent waters to a GAC column tend to fluctuate with seasonal changes in the weather.
5. Although most of the organisms isolated from the GAC in each column were not pathenogenic some are classified as opportunistic pathenogens. The

fact that some coliform groups were present in the effluents of the columns toward the end of the study suggests that other pathenogens may be present.

6. The dominant genera of bacteria isolated from the GAC columns are:

- a. Achromobacter
- b. Acinetobacter
- c. Aeromonas
- d. Alcalingenes
- e. Bacillus
- f. Chromabacterium
- g. Corynebacterium
- h. Micrococcus
- i. Microcylus
- j. Paracoccus
- k. Pseudomonas

Analysis and Discussion of Chemical Data

In the following sections the chemical data obtained in the pilot study will be analyzed and interpreted with the following objectives in mind:

1. to understand the mechanisms for the removal of TOC and THMFP on GAC columns; more specifically, to distinguish the roles of physical adsorption and microbiological degradation on the columns.
2. to evaluate the rates of microbiological processes on GAC columns and to compare these with other literature values.
3. to contrast the effectiveness of GAC columns which receive waters which have been ozonated with those which receive unozonated influent.

Cumulative Removal Plots--

Figures 39-40 and 41-42 show plots of cumulative THMFP and TOC removed as a function of both time and bed volumes of water processed. These curves are instructive in that their slopes give values for the rates of removal of THMFP and TOC. Figures 43-44 are plots of cumulative THMFP removed vs. cumulative THMFP influent, each in units of grams of THMFP. Figures 45-46 are corresponding plots in terms of kilograms of TOC removed and TOC influent. Among others, Benedek (51) has pointed out the value of plots of this type in that the slope at any point is the fraction of THMFP (or TOC) removed at the time that point was taken. It should be noted, however, that neither axis relates to time directly so two points at a given x coordinate were not necessarily taken at the same time. Figures 47 and 48 compare GAC column sets 5-6 and 3-4 with respect to cumulative THMFP and TOC removal, for the purpose of contrasting the non-ozonated and

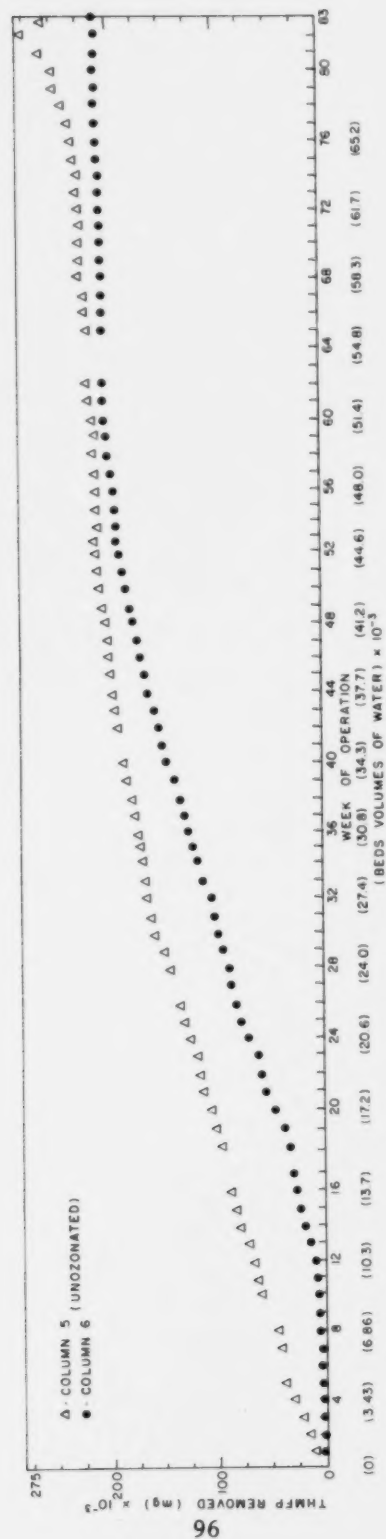


Figure 39. Cumulative Removal of Trihalomethane Formation Potential of Settled - Filtered Water by GAC Columns.

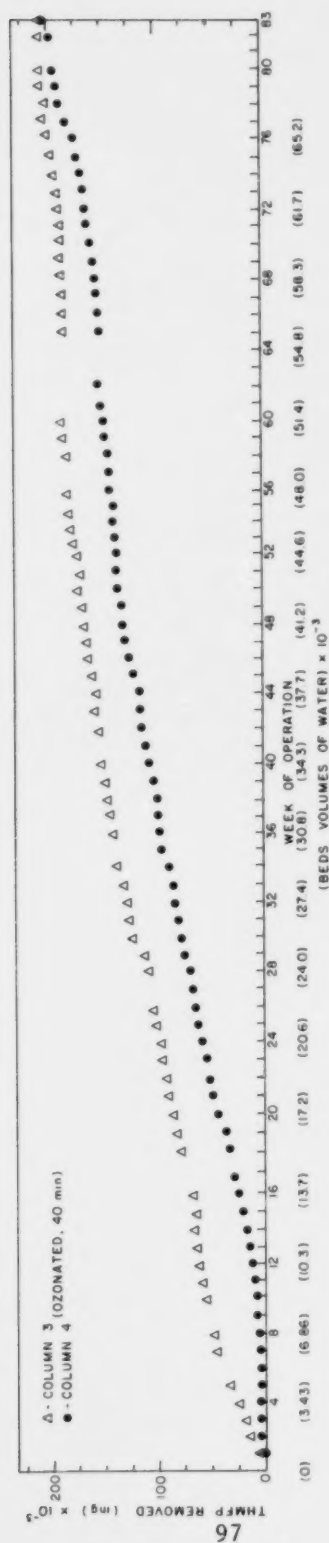


Figure 40. Cumulative Removal of Trihalomethane Formation Potential of Long Contact Time Ozonated Water by GAC Columns.

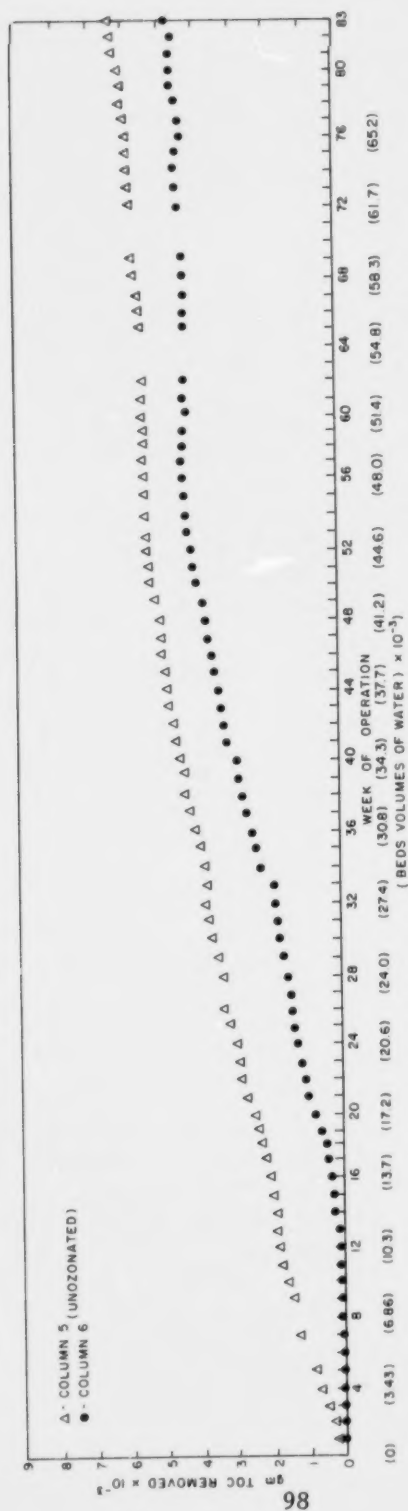


Figure 41. Cumulative Removal of Total Organic Carbon of Settled - Filtered Water by GAC Columns.

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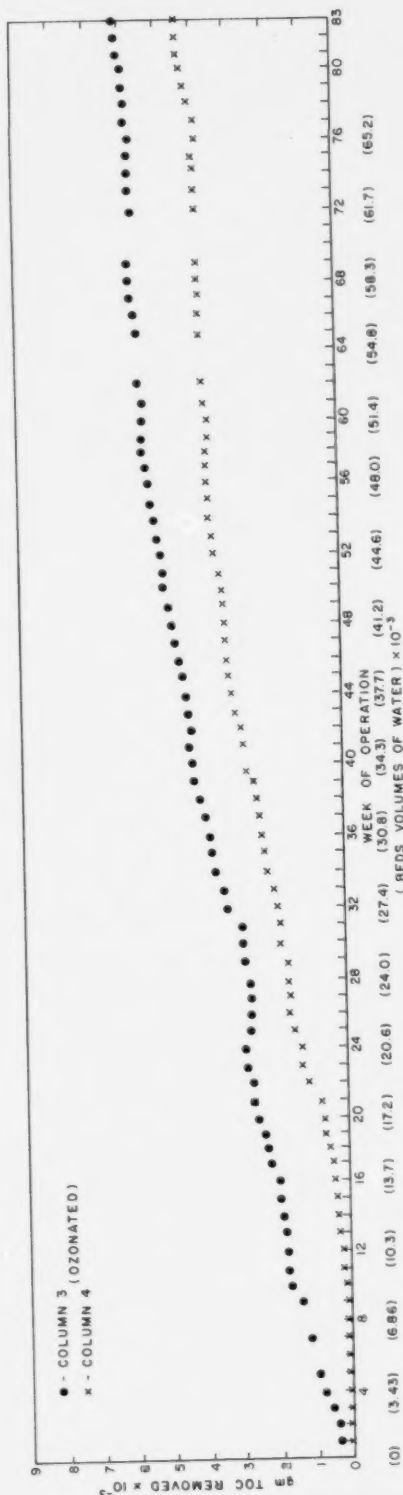


Figure 42. Cumulative Removal of Total Organic Carbon of Long Contact Time Ozonated Water by GAC Columns.

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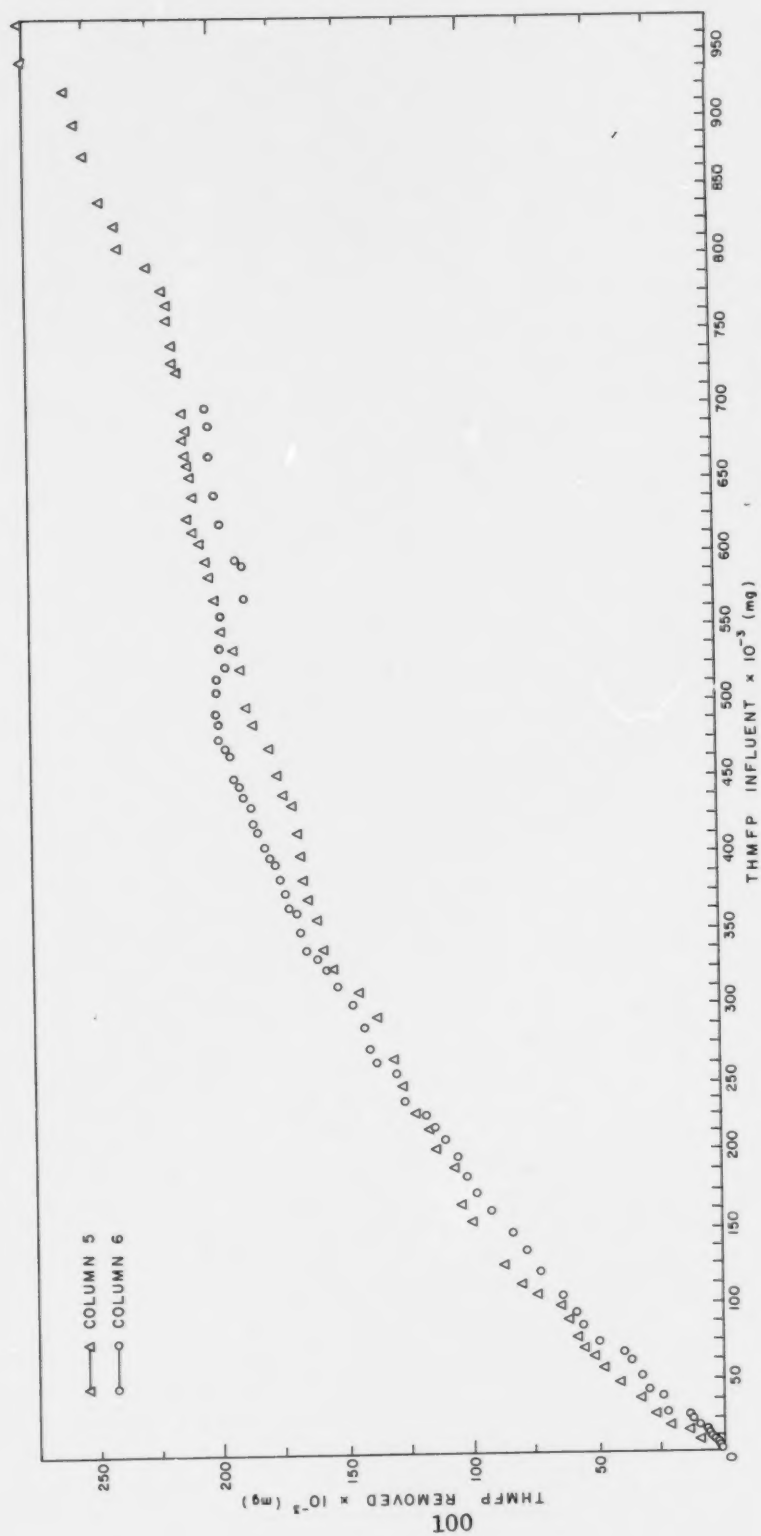


Figure 43. Cumulative Removal to Cumulative Influx of Trihalomethane Formation Potential of Settled - Filtered Water by GAC Columns.

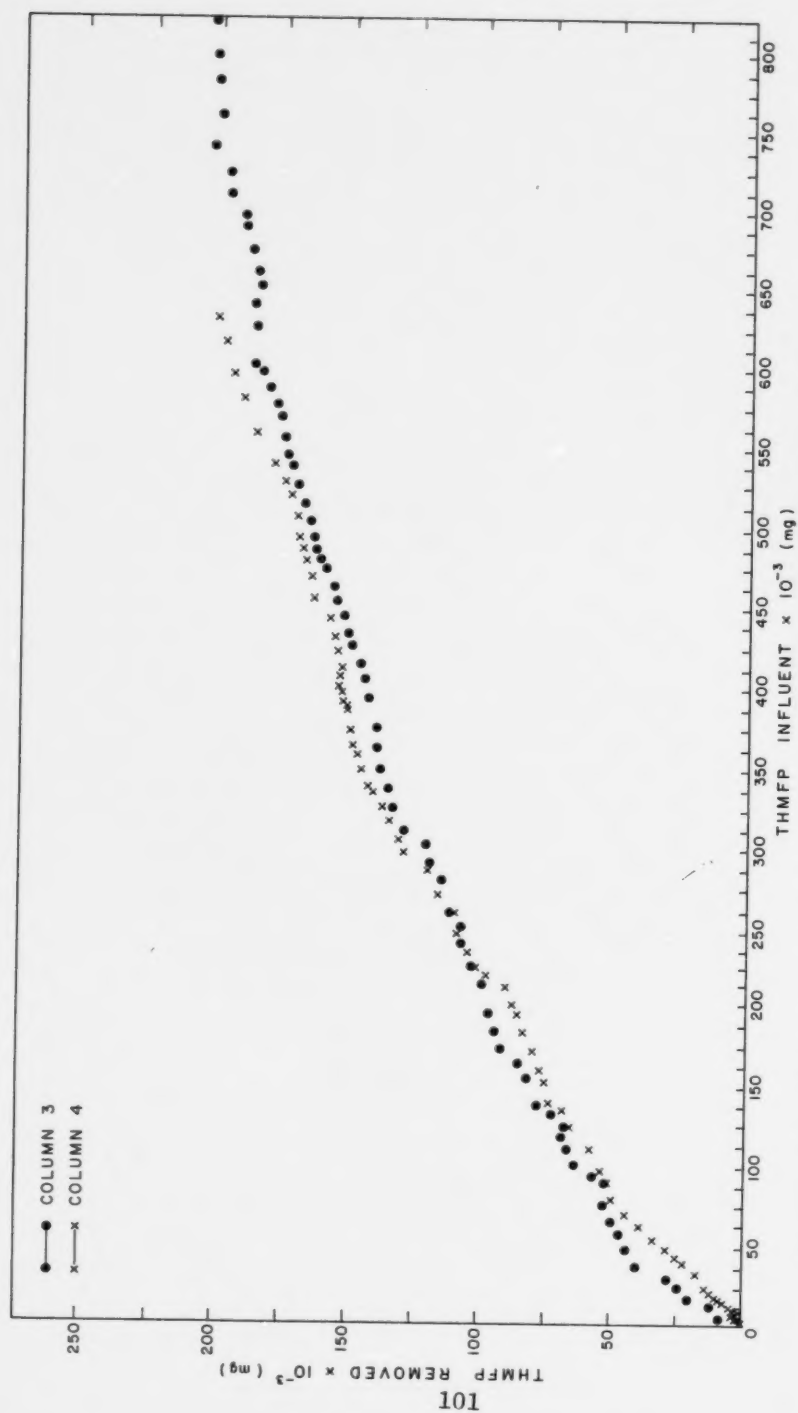


Figure 44. Cumulative Removal to Cumulative Influx of Trihalomethane Formation Potential of Long Contact Time Ozonated Water by GAC Columns.

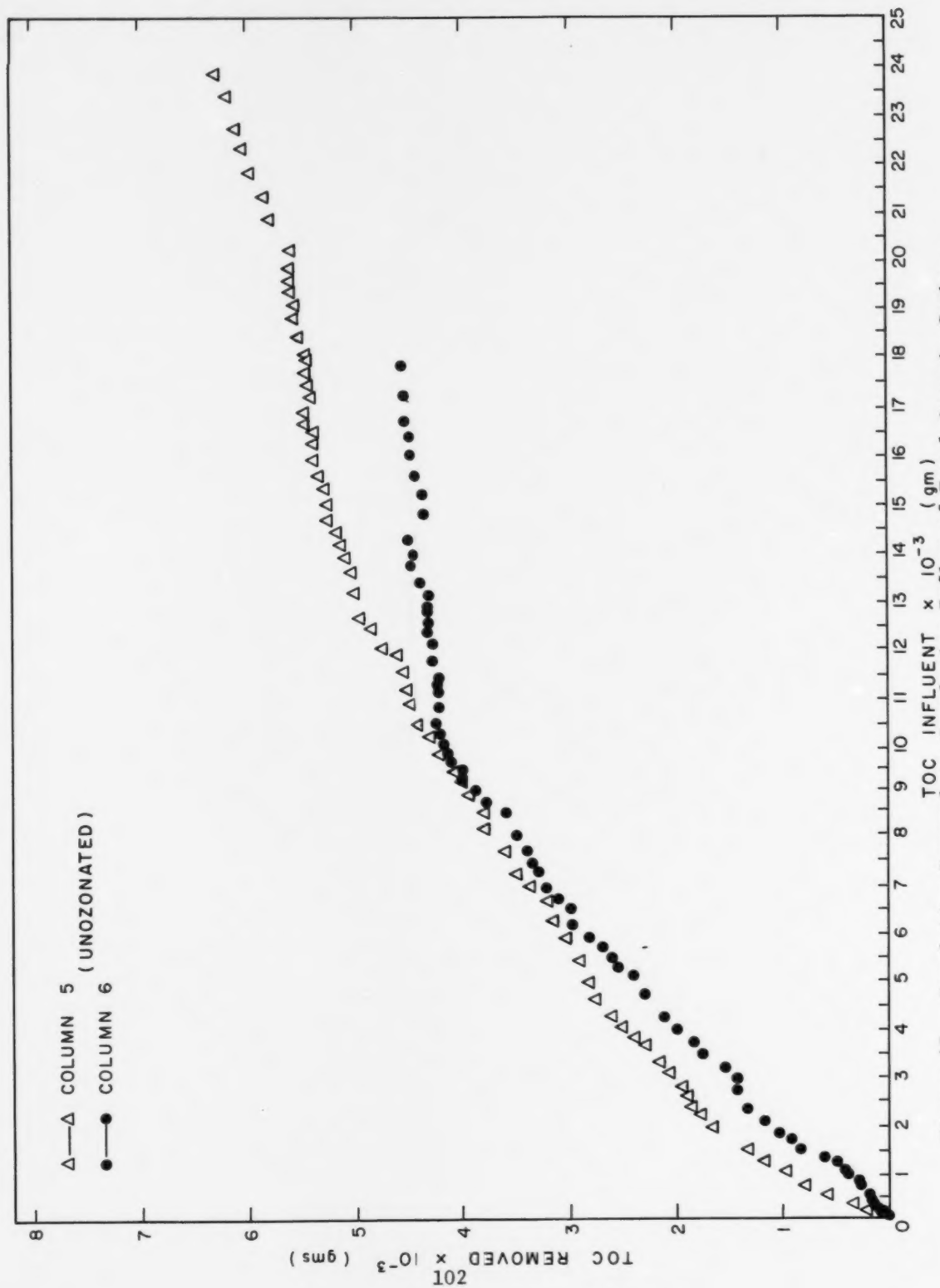


Figure 45. Cumulative Removal to Cumulative Influx of Total Organic Carbon of Settled - Filtered Water by GAC Columns

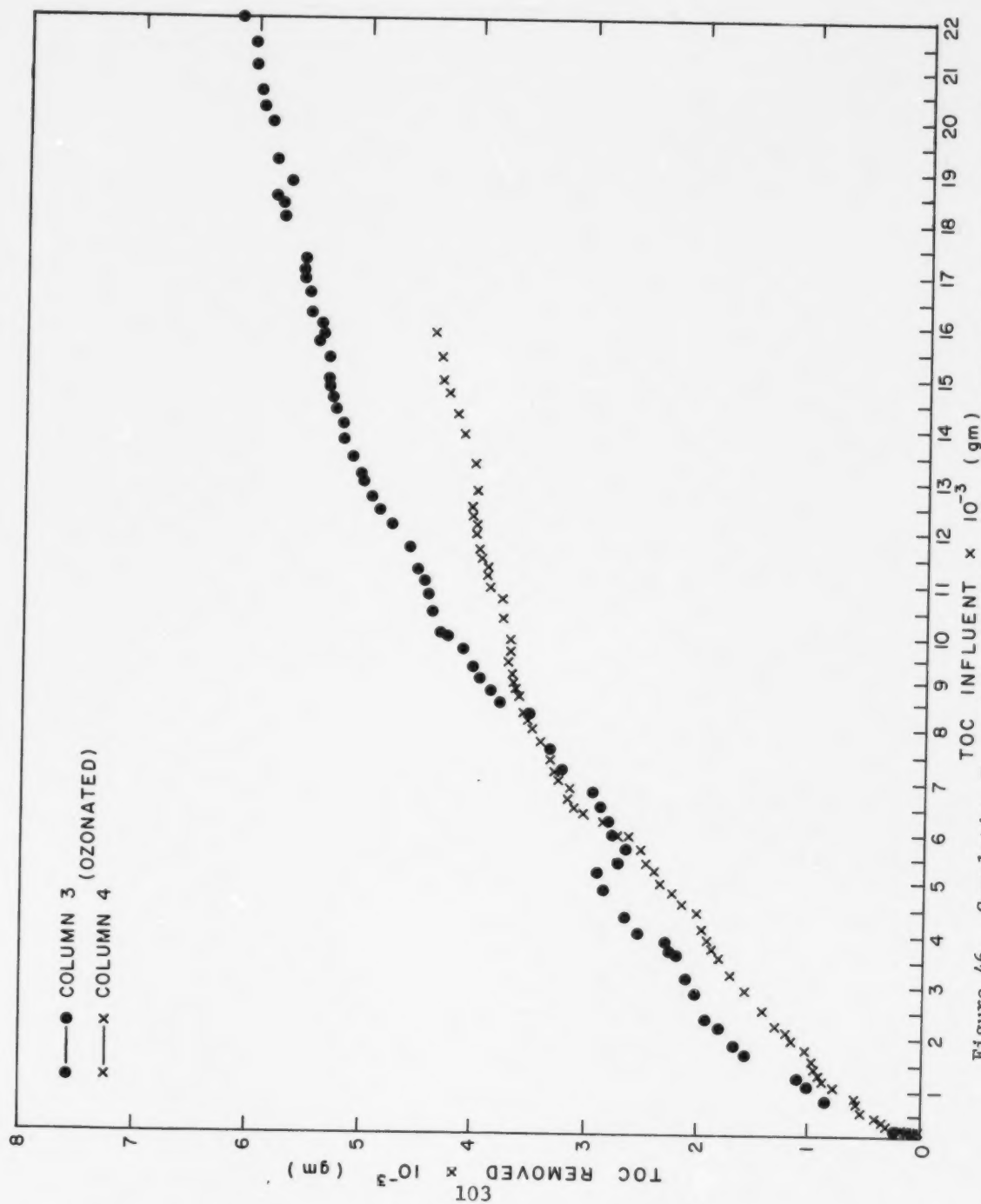


Figure 46. Cumulative Removal to Cumulative Influx of Total Organic Carbon of Long Contact Time Ozonated Water by GAC Columns.

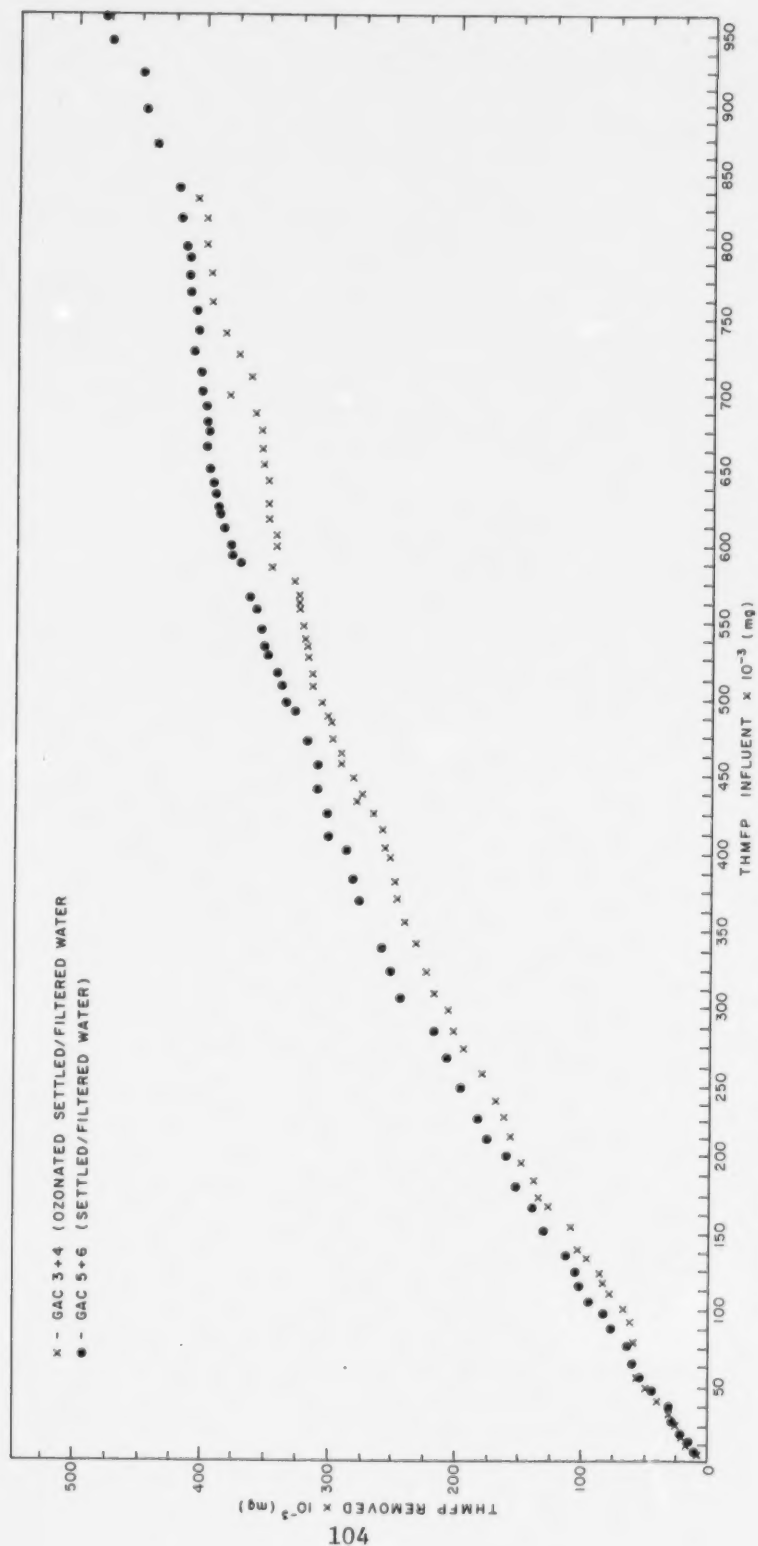


Figure 47. Cumulative Removal to Cumulative Influx of Trihalomethane Formation Potential of Settled - Filtered Water and Long Contact Time Ozonated Water by Sets of GAC Columns.

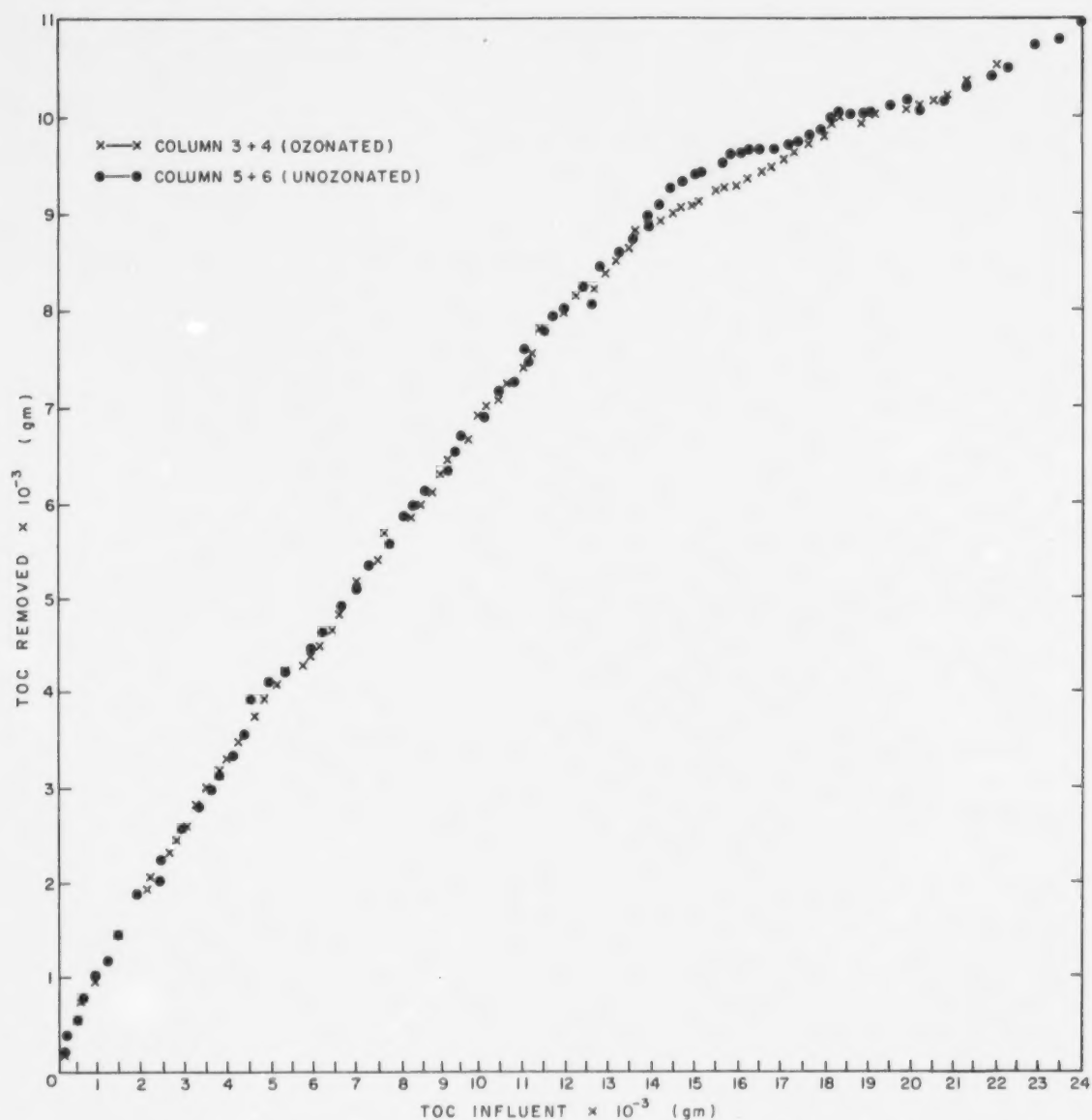


Figure 48. Cumulative Removal to Cumulative Influx of Total Organic Carbon of Settled - Filtered Water and Long Contact Time Ozonated Water by Sets of GAC Columns.

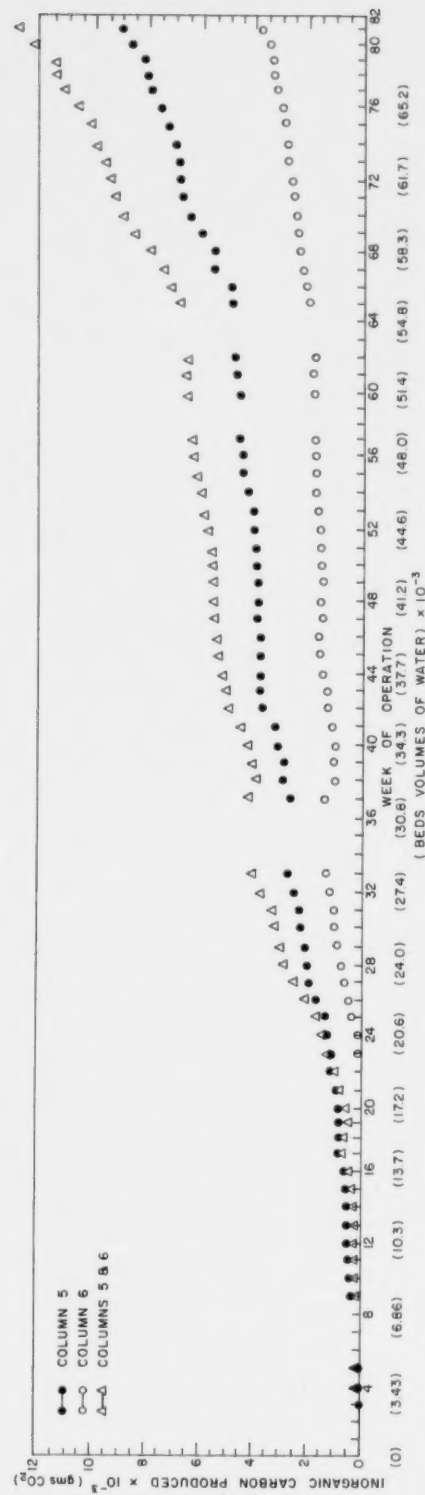


Figure 49. Cumulative Production of Inorganic Carbon in Settled - Filtered Water by GAC Columns.

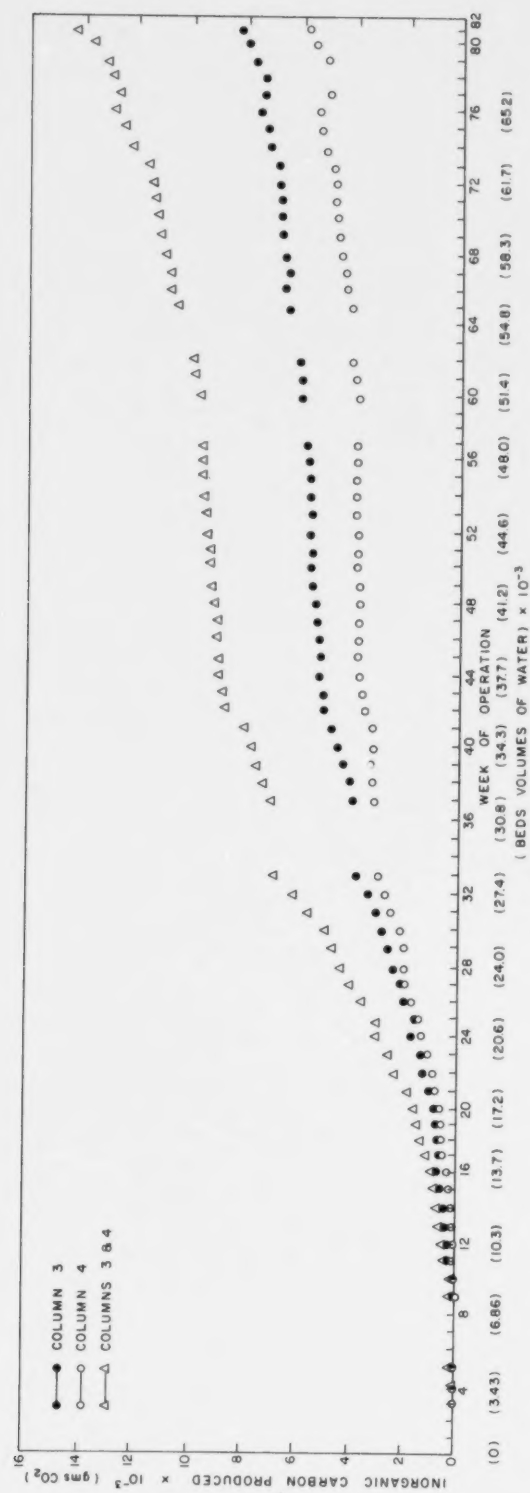


Figure 50. Cumulative Production of Inorganic Carbon in Long Contact Time Ozonated Water by GAC Columns.

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ozonated streams respectively. Figures 49-50 give plots of cumulative inorganic carbon produced across the GAC columns.

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Analysis of Four Operational Periods of Pilot GAC Columns--The operational phase of the GAC pilot plant may be divided into four periods for the convenience of discussion.

Period A (week 0-21). The period of initial service during which each pair of columns remove eighty percent or greater of the influent TOC or THMFP. During this period INC release from the columns is extremely low, although it is increasing toward the end of the period.

Period B (week 22-52). The period referred to earlier as the pseudo steady-state period. During this time removal of TOC and THMFP is somewhat lower (50-60%) and carbon dioxide production is quite high. During the last few weeks of this period removal rates decline precipitously as winter sets in.

Period C (week 52-62). The colder weeks of the winter of 1980-81, during which removal rates are erratic and low, and CO₂ production is very small.

Period D (week 65-83). The period after restart of the pilot plant and through July 1981, characterized by high CO₂ production and removal rates higher than the winter period but lower than Period B.

For each of these periods Table 12 gives the rates of removal expressed in terms of moles of TOC or millimoles of THMFP removed per cubic meter of GAC per hour, or moles of CO₂ produced per cubic meter of GAC per hour. In addition, Table 12 tabulates the fraction of TOC and THMFP removed in each period (f-TOC and f-THMFP respectively).

Table 12 and the body of data presented before suggest the following conclusions may be drawn regarding the performance of the GAC columns in the Shreveport pilot plant.

1. At the outset of this study, GAC columns receiving both ozonated and unozonated water appear to function in a mostly physical mode, presumably by a film diffusion controlled process (34). The rate of removal of TOC and THMFP is not quite quantitative during this period, perhaps due to a small amount (10%) of non-adsorbable TOC which is present in the Waterboy effluent.

2. The first column in each set begins breakthrough after approximately 8-10 weeks in operation. Carbon dioxide production is not appreciable during the first 21 weeks and the process is probably still largely adsorption. The gradual diminution of rate of removal during the ensuing period is presumably due to the saturation of macropore sites and the onset of pore diffusion-limited kinetics (34) at least in the first columns of the sets (figures 39-43).

3. During the period from week 22 to 44 increased carbon dioxide production is observed (Figures 49-50 and Table 12) indicating the presence of microbial respiration processes in the GAC columns. The absence of CO₂

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TABLE 12. RATE PROCESSES IN PILOT SCALE GAC COLUMNS: SHREVEPORT, LA.

WEEK	Moles TOC/m ³ GAC-hr. #			Moles CO ₂ /m ³ GAC-hr #			mMoles TTHMFP/m ³ GAC-hr #			f-TOC*		f-TTHMFP*	
	GAC	O ₃ -GAC		GAC	O ₃ -GAC		GAC	O ₃ -GAC		GAC	O ₃ -GAC	GAC	O ₃ -GAC
0-21	0.54	0.52		0.04	0.09		2.04	1.65		0.82	0.83	0.83	0.79
22-52	0.53	0.48		0.13	0.20		1.84	1.60		0.55	0.55	0.56	0.53
53-62	0.075	0.14		0.07	0.07		0.43	0.53		0.10	0.19	0.19	0.26
65-83	0.26	0.26		0.28	0.20		0.99	1.00		0.24	0.27	0.24	0.30

* f=fraction of TOC and THMFP removed, averaged over period

Values obtained from cumulative TOC and THMFP removed or carbon dioxide produced, divided by 0.178 m³ GAC per pair of columns and the time period. When data were unavailable due to instrument failure, etc. the number of weeks used in the calculation was decreased accordingly. That is, the procedure was equivalent to taking the columns off-line for that week.

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production before this period may be due to the requirement to saturate the GAC surface with CO₂, but it is also probably related to slower microbial respiration at the cooler water temperatures (11-14°C) prevalent before week 15 (Figure 30).

4. The occurrence of biosynthesis on the GAC columns is confirmed by modified total plate counts of influent and effluent water during weeks 0-22, especially of the ozonated columns (Table 5). These data speak against endogenous respiration as the only mechanism for carbon dioxide production, although this must be a contributing process.

5. During the period between weeks 22 and 44 two processes appear to be operating to remove carbonaceous material from the water, adsorption and microbiological degradation. If the rate of CO₂ production is taken as a direct measure of microbial activity, this mechanism is responsible for an average of 30%-40% of the TOC removal during this period. As this period ends both processes decline in rate, the adsorption process because of continued diminution in the number of active sites, and the microbiological process because of decreasing water temperatures.

6. Beyond approximately week 44 microbiological processes appear to become increasingly important relative to physical processes. With the advent of cold water temperatures in late 1980 virtual cessation of CO₂ production is observed to occur, and by approximately week 52, TOC removal in both ozonated and unozonated columns has dropped to values approximately one-half to one-fourth of those observed even during weeks 40-50. THMFP removal does not decline quite so dramatically, but a substantial diminution is observed as compared to the fall period (Table 12).

7. Upon resumption of testing at week 65 (the week of March 17) column sets 5-6 and 3-4 are observed to resume TOC and THMFP removal. Indeed, removal accelerates to values two to three times those observed in the winter period, a clear indication that microbial processes have become the dominant mechanism (Table 12).

8. Viable bacteria populations are observed to be in the range of 50 x 10⁶ CFU per gram of dry weight GAC at restart, and rise to two to six times this value in the spring and summer months of 1981 (Table 7). This observation, combined with the increase in carbon dioxide production on the columns (Table 12 and Figures 49-50), confirms the predominance of a biologically controlled process during approximately the last thirty to forty weeks of the pilot columns. During this period the average rate of carbon dioxide production is approximately equal to the rate of TOC removal on a molar basis. The equivalence of these values suggests a process occurs in the GAC columns in which carbon (natural TOC, not GAC) is metabolized to CO₂. It should be noted, however, only about twenty percent of the influent TOC is metabolized to CO₂; that is, not all of the natural organic carbon compounds in the lake are biodegradable in the time frame available in the columns (24 minutes EBCT).

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9. During the last weeks of the project when biological mechanisms apparently predominate, microbial populations appear to be greater in the

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first column of a set (Table 7). This trend was not observed the previous summer and fall, although the data base there is not too extensive. In general modified plate counts and ATP values show higher biomasses present in the columns in the summer of 1981 than in 1980. Figures 27 and 29 show that more TOC removal occurs in the first column during this period, more so for the non-ozonated than the ozonated columns.

10. The rate of TOC removal during weeks 65-83 (0.26 moles of TOC/m³-hr.) is comparable to the values reported by other workers for BAC processes. Eberhardt has stated that bacteria in GAC columns should be capable of removal rates of 0.08-0.33 moles of TOC/m³-hr. (48). In the DÜsseldorf study, Poggenburg *et al.* (46) report data which can be used to calculate a removal rate of 0.8 moles TOC/m³-hr., but since the GAC columns had been in service only 250 days, some adsorption is probably still occurring at this time. Rice *et al.* (44) report a biological rate of 0.35-0.49 moles TOC/m³-hr. was achieved at the Bremen plant.

11. During the last operational period (weeks 65-83) THMFP values of the water from GAC columns receiving both unozonated and ozonated water (sample sites 7 and 14 respectively) exceed the 0.10 mg/L criterion in all but a few cases. Microbial removal rates of approximately 0.26 moles of TOC/m³ GAC-hr. are not sufficient to handle the large concentrations of organics influent to the GAC column. In order to meet this criterion reactivation would be required for the column sets, or at least one column of each pair, at approximately week 52-67.

In summary, the data obtained in the GAC pilot study may be understood by invoking a combination of three mechanisms for removal of natural organics from Cross Lake water:

- a. adsorption onto macropore sites on the GAC surface,
- b. adsorption onto micropore sites on the GAC surface,
- c. microbiological metabolism.

In the initial weeks of service of the GAC columns mechanism a. clearly predominates. However, after only a few weeks the evidence suggests that macropore sites are becoming saturated, and removal is limited to mechanisms b. and c. after 30-40 weeks of service. By approximately the 52 week, essentially only microbial metabolism is operative and the rate of THMFP removal is not sufficient to meet a 0.10 mg/L criterion.

The Effect of Preozonation on GAC Performance--An important objective of this project was to contrast the effectiveness of GAC columns receiving ozonated water with identically packed columns receiving unozonated water.

There are several ways in which one may address this question. One could first look at the overall removal in GAC versus O₃/GAC trains for the lifetime of the project. Table 13 presents such a comparison, from which it is clear that the O₃/GAC system outperforms the GAC system only because of the oxidation that occurs in the O₃ contact and retention

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TABLE 13. TOTAL CUMULATIVE PERFORMANCE DATA FOR GAC COLUMNS: SHREVEPORT, LA.

COL. NO.	OZONE TREATED	TOTAL CUM. TOC*	INFLUENT THMFP #	TOTAL CUM. REMOVED TOC * THMFP #	% OF TOTAL INF. REMOVED		OXIDANT [@]		TOT. % REMOVED	
					TOC	THMFP	TOC	THMFP	TOC	THMFP
5	NO	24.17	969	6.23	25.8	26.6	---	---	25.8	26.6
6	NO	17.94	711	4.70	26.1	30.1	---	---	26.1	30.1
5+6	NO	24.17	969	10.93	45.2	48.7	---	---	45.2	48.7
3	YES	22.04	830	6.10	27.7	24.6	2.13	139	36.5	50.8
4	YES	15.94	626	4.38	27.5	31.9	2.13	139	36.3	50.6
3+4	YES	22.04	830	10.48	47.5	48.7	2.13	139	52.2	56.0

* Kg TOC; # g TTHMFP; @ Amount of TOC (Kg) and THMFP (g) removed in ozone contactor and detention basin. Data cover entire project period of 81 weeks.

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chambers. That is, cumulative removal of both THMFP and TOC in the GAC columns per se is less for the preozonated columns than for the unozonated columns. This is an inadequate comparison, however for two reasons. Firstly, less TOC and THMFP are influent to the O₃/GAC columns due to the effect of oxidation. When one takes this into account by using the measure "% of Total Influent Removed", it is seen that the O₃/GAC and GAC systems perform almost identically over the whole project period. Secondly, it is now almost certain that both adsorption and microbiological mechanisms operate in the GAC columns (see previous section). Thus, an overview of removal in the GAC columns over the entire project may be misleading. Rather, one should attempt to answer two important questions which are corollaries to the original objective; viz:

1. does preozonation enhance physical adsorption of natural organics from Cross Lake?
2. does preozonation enhance microbiological metabolism of the same matrix?

Evidence pertinent to the resolution of both these issues has been obtained during this project. Toward the resolution of 1, isotherm studies not reported in detail here show that preozonation decreases the adsorbability of Cross Lake organics (C.-C. Lin, The University of Texas at Dallas, to be published). However, the difference is slight, at least with the ozone doses used in this study, and as Figure 48 and Table 12 show, cumulative removal of the ozonated organics (TOC) tracks very closely the removal of the unozonated organics. There is some discrimination evident in Figure 47, relating to removal of THMFP, but even so there is not a major effect of ozonation on adsorbability.

The question of the effect of ozone on microbial degradability may be answered by referring to the pilot plant data taken during weeks 65 - 83. During this period the plant is operating in essentially a microbiological mode, as noted above. As shown in Table 12 rates of TOC and THMFP for the GAC and O₃/GAC trains are essentially the same. Again, however, it should be recognized that the concentration of organics in the O₃/GAC stream is less than in the GAC stream. For this reason, there appears to be a slight excess in the fraction of TOC and THMFP removed in the ozonated stream during the period (columns f-TOC and f-THMFP). In order to examine this question more completely, a statistical analysis of the TOC and THMFP removal data was conducted for period 4 (weeks 65-83). First, THMFP effluent/influent ratios for column 5-6 and 3-4 were subjected to pairwise t-testing. Note that for the period this ratio has means of 0.76 and 0.70 for GAC and O₃/GAC streams, with standard deviations of 0.12 and 0.10 respectively. On the surface, it would appear they are not statistically different. However, pairwise t-testing of the data gave a t value (n-1 = 17) of 2.611, well outside of the 95% confidence limit for rejection of the null hypothesis. In other words, the two groups of effluent-influent ratios for GAC and O₃/GAC columns do not appear to have the same mean. In addition, if one utilizes non-pairwise testing for the data set, one can show 95% confidence in at least a difference in means of 0.10. That is, the O₃/GAC train is shown to give 10% better removal than

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the GAC train at the 95% confidence limit.

For removal of TOC the data are not quite as conclusive. Analysis of the effluent/influent data for columns 5-6 and 3-4 show means of 0.76 ($\sigma = 0.09$) and 0.73 ($\sigma = 0.12$) respectively. Pairwise t-testing of the data do not show a difference at the 95% confidence level, but do show a difference at the 90% level.

Analysis of the THMFP data was also carried out by computing the first order rate of removal on a week by week basis. First order removal is defined here as the amount of THMFP removed in a week divided by the amount of THMFP influent to the column in that week. Pairwise t-testing of this data for GAC and O_3 /GAC systems did not show a statistically significant difference in the two trains at the 95% confidence level. However, at the 90% level the difference was significant.

In summary, the statistical analysis lends more credence to the assumption that preozonation appears to have a slight positive effect on the removal of Cross Lake natural organics in GAC columns. The consequences of this effect will now be examined in terms of the two treatment trains, GAC and O_3 /GAC to meet an arbitrary THMFP criterion.

The Overall Effect of Ozonation on Treatment of THMFP--A close examination of the figures shown in this report, and the THMFP data in particular, suggests the following conclusions with regard to the overall effect of ozonation in removal of THMFP in filter plants to which GAC columns are added:

Firstly, it appears that preozonation "flattens" the pseudo steady-state period which characterizes GAC treatment. As shown in Figures 24 - 26, the GAC effluent seems to show THMFP values which gradually rise throughout this period, while the values for the O_3 /GAC train seem to reach a flatter plateau. In retrospect, we now realize this is due to slightly more effective microbial removal in the O_3 /GAC train at a time when adsorption is dropping off continually.

Secondly, during the winter months when treatment is poorer overall, ozonation leads to more efficient treatment (Table 12). This apparently is due to both chemical oxidation and encouragement of microbiological oxidation. In the weeks subsequent to the adsorption period, the result is consistently lower THMFP values for the O_3 /GAC vs. the GAC stream. For the period from week 44 to week 62, THMFP averaged 82 $\mu\text{g/L}$ (σ 17) in the GAC train and only 68 $\mu\text{g/L}$ (σ 15) in the O_3 /GAC train. For the entire "microbiological" phase, weeks 45 to 83, the THMFP mean values in the effluents were 118 (σ 58) for the GAC train and 96 (σ 43) for the O_3 /GAC. In the following section costs associated with full-scale O_3 /GAC and GAC systems will be evaluated for the purpose of placing the apparent benefits of ozonation into a fiscal perspective. In that section it will be assumed that ozonation can extend the "lifetime" of GAC columns, i.e. the time in service before reactivation is required. While this increment of lifetime is not precisely established by this study, for the doses of ozone used it appears to be approximately 25%, namely the increase in lifetime to

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approximately 1.25 years from approximately one year for GAC alone.

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DISCUSSION OF PHASE I-E-2 RESULTS

In March of 1981, four new columns were placed on line in the pilot treatment plant (Table 10) in an experimental phase referred to as I-E-2. The columns, two sand and two GAC, were installed in order to provide more detailed microbiological and chemical data, particularly during the first few weeks after installation.

Figures 51 - 58 show cumulative removal data in terms of THMFP and TOC, and figures 59 - 62 show cumulative CO₂ production during the seventeen week test period. Table 14 is a summary of removal rates in the 1981 period, and should be compared to a similar compilation for the 1980 period in Table 12. Microbiological data for these columns have been discussed previously.

The following observations of interest may be made from these data:

1. The rates of removal of TOC and THMFP on the fresh GAC columns are greater in the 1981 test period than in weeks 0-21 of the first part of the pilot study. This is primarily a reflection of the higher concentrations of organics in the lake in the summer of 1981 versus the winter and spring of 1980. Average TOC values at site 5 (the Waterboy effluent) were 5.0 mg/L and 2.8 mg/L respectively during these periods.

2. Figures 53 and 56 compare cumulative THMFP and TOC removal of the GAC columns receiving ozonated and unozonated water. It is clear from both figures that the unozonated and ozonated streams are treated with almost equal efficiency during the early stages of the study, but the ozonated stream lags behind at the end. (It should be recalled that the slopes of plots 51 - 58 give the fraction of TOC or THMFP removed during the treatment period). As noted in earlier parts of Section 6, this relative deficiency of the O₃/GAC train is probably due to the poorer adsorbability of natural organics after mild oxidation.

3. Figures 51 and 52 illustrate the superiority of GAC over sand filters for the removal of THMFP. In the case of unozonated sand, removal apparently begins to accelerate in the tenth to twelfth week due to microbial action, but the effect is not seen in the ozonated sand columns. Unfortunately two weeks of data at the end of the experiment were not obtained, so it is not clear if removal would have commenced by week 17. The apparent superiority of the unozonated sand columns may be due to "disinfection" of the ozonated columns; however, the MTPC data do not confirm this postulate (see below). That the ozonated water is less biodegradable is difficult to accept.

4. Modified total plate count data in Figure 36 attest to the fact that microbial populations build up very quickly on GAC and sand surfaces; however they are an order of magnitude lower than those found in columns 5-6 and 3-4 during the same period, 1981 (compare figure 36 and Table 7).

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ATP values are also greater in columns 5-6 and 3-4 by the same factor of 10

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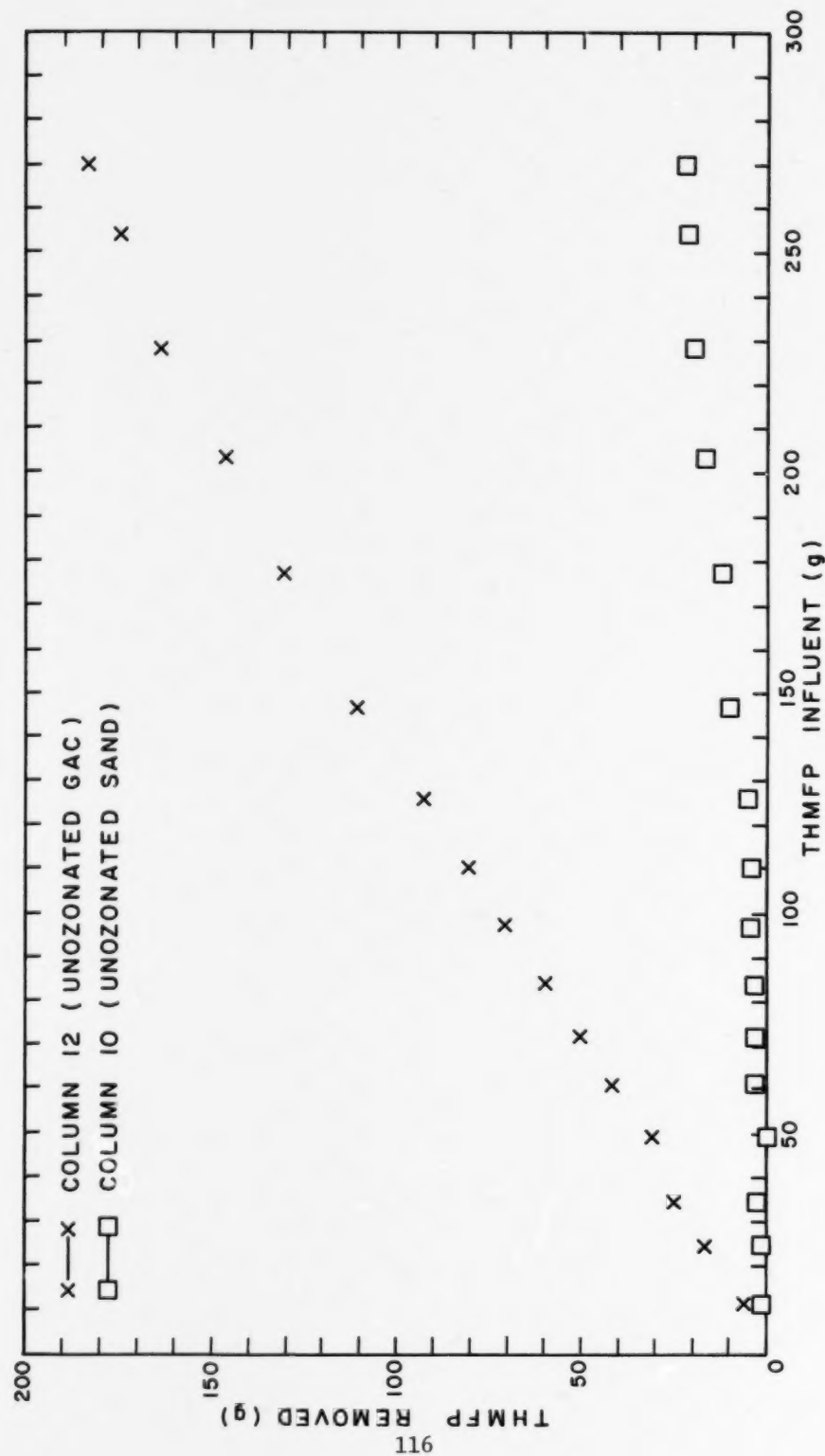


Figure 51. THM Formation Potential Removed in Phase I-E-2, Columns 12 and 10.

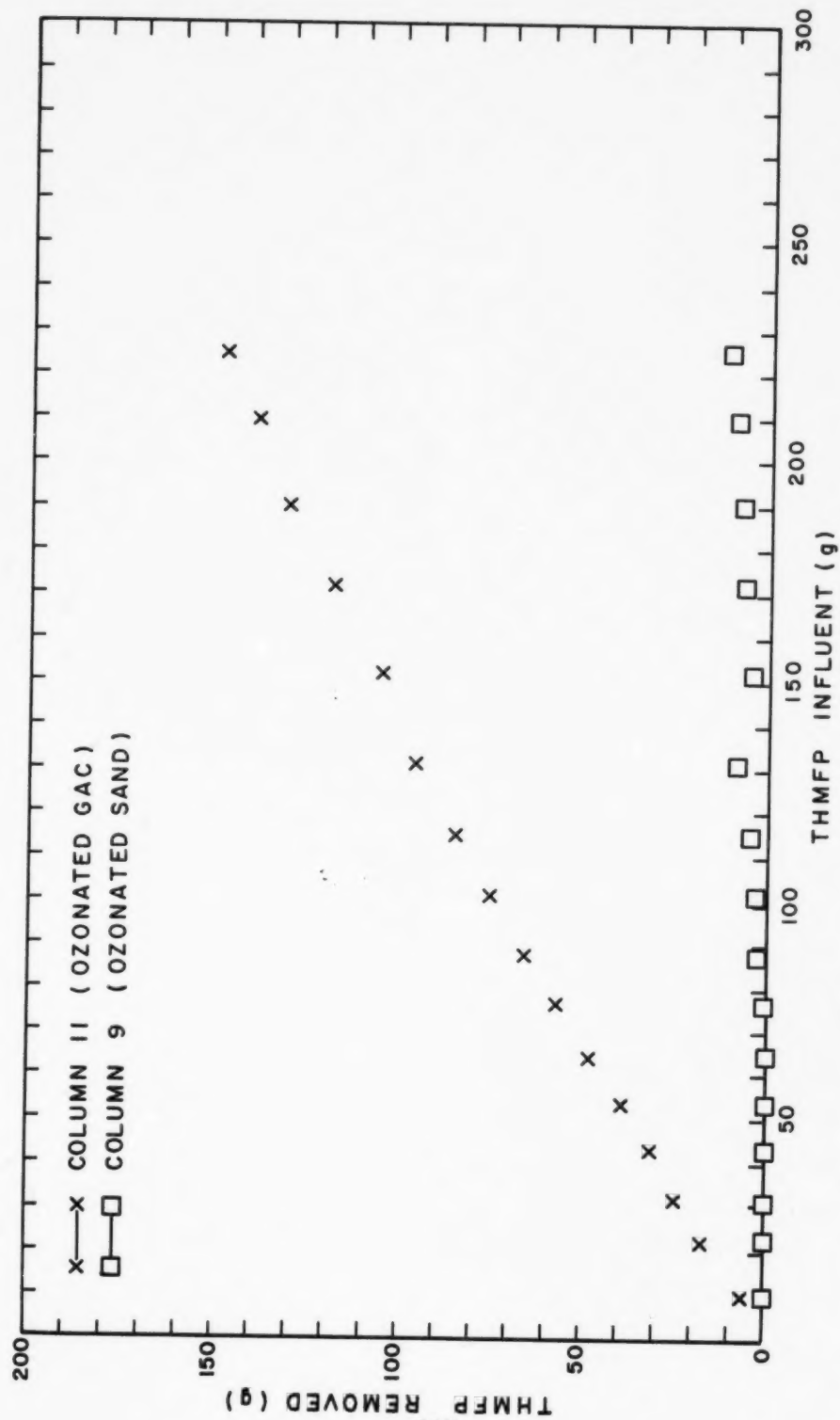


Figure 52. THM Formation Potential Removed in Phase I-E-2, Columns 11 and 9.

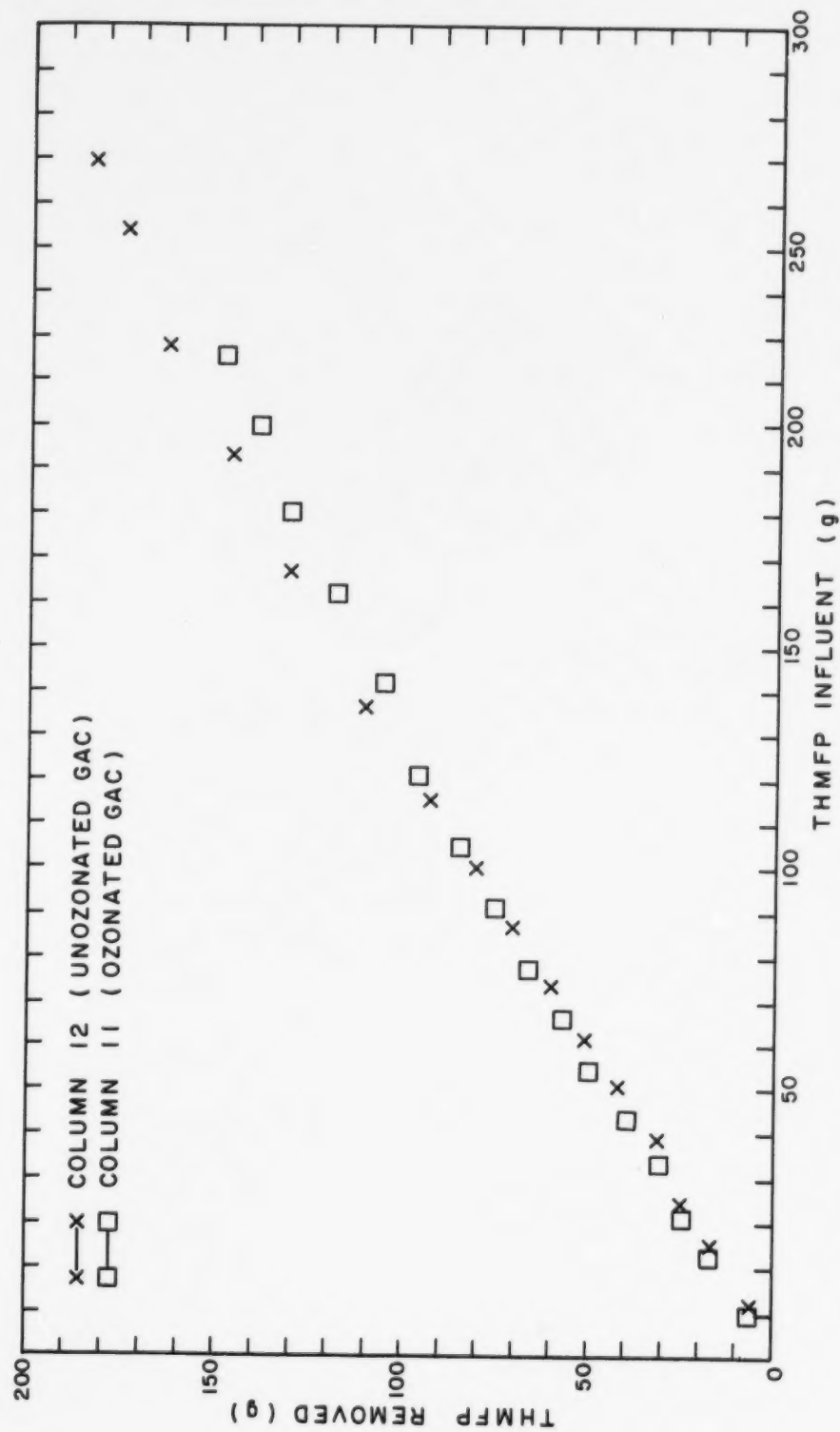


Figure 53. THM Formation Potential Removed in Phase I-E-2, Columns 12 and 11.

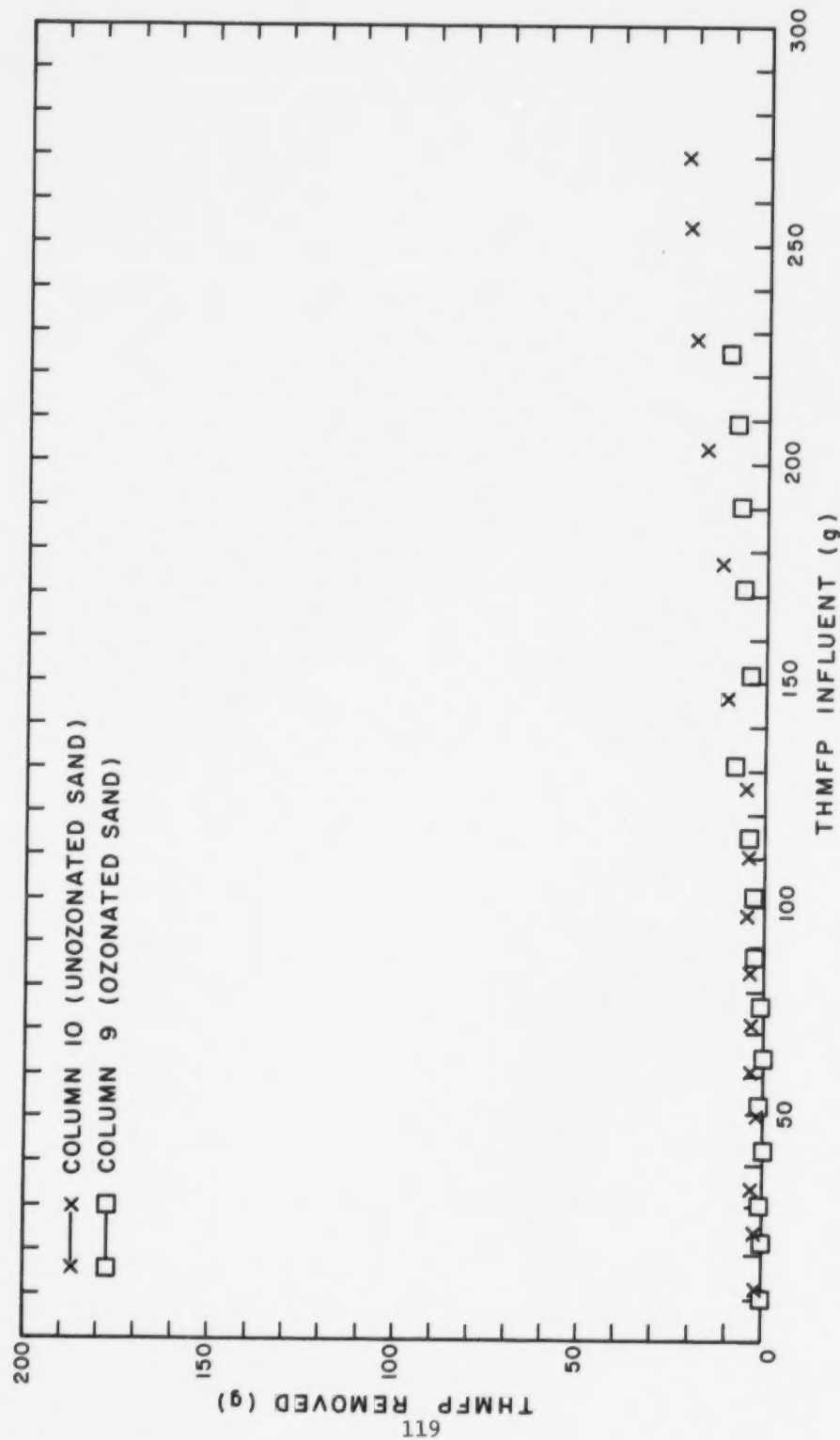


Figure 54. THM Formation Potential Removed in Phase I-E-2, Columns 10 and 9.

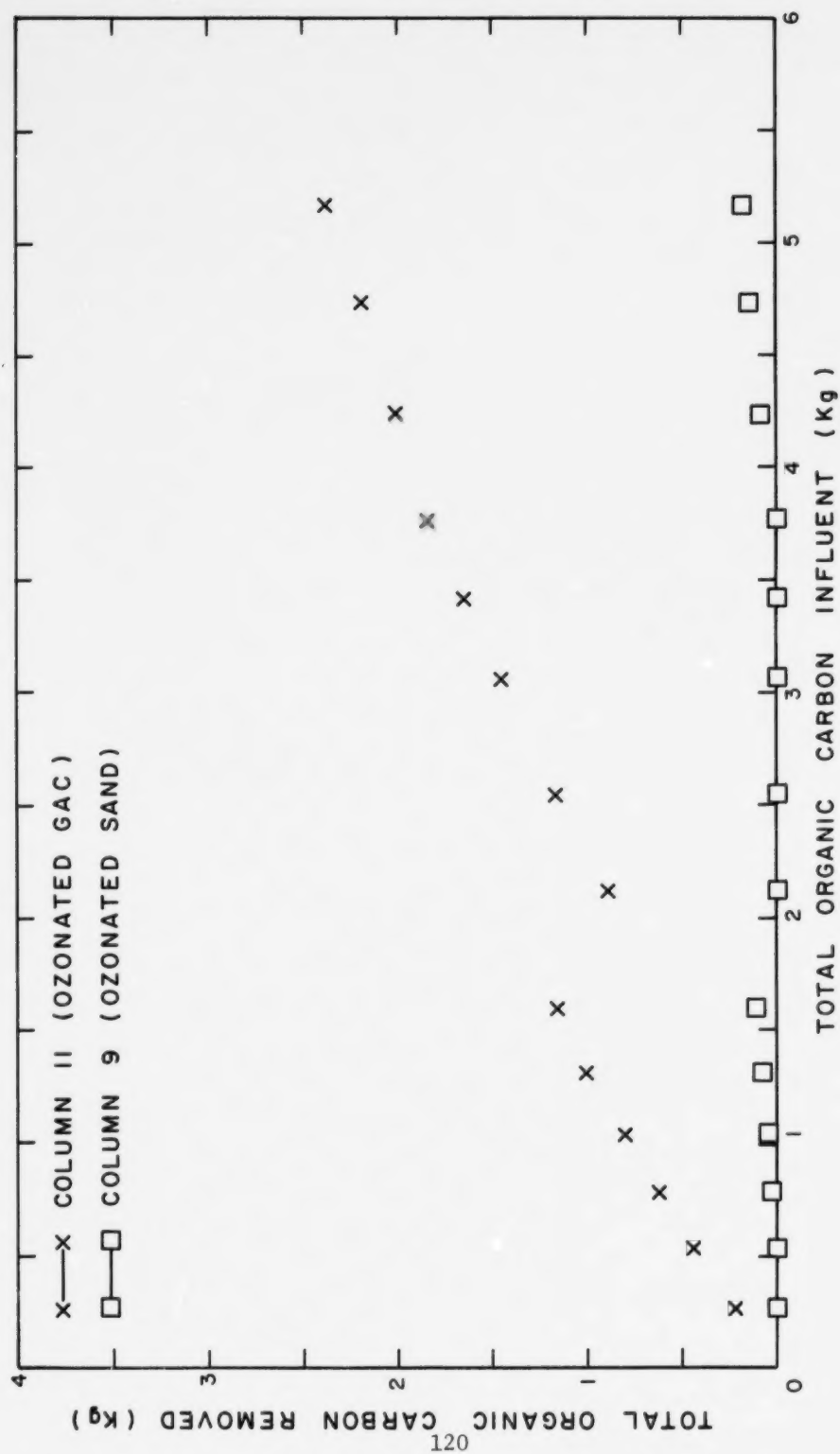


Figure 55. Total Organic Carbon Removed in Phase I-E-2 Study, Columns 11 and 9.

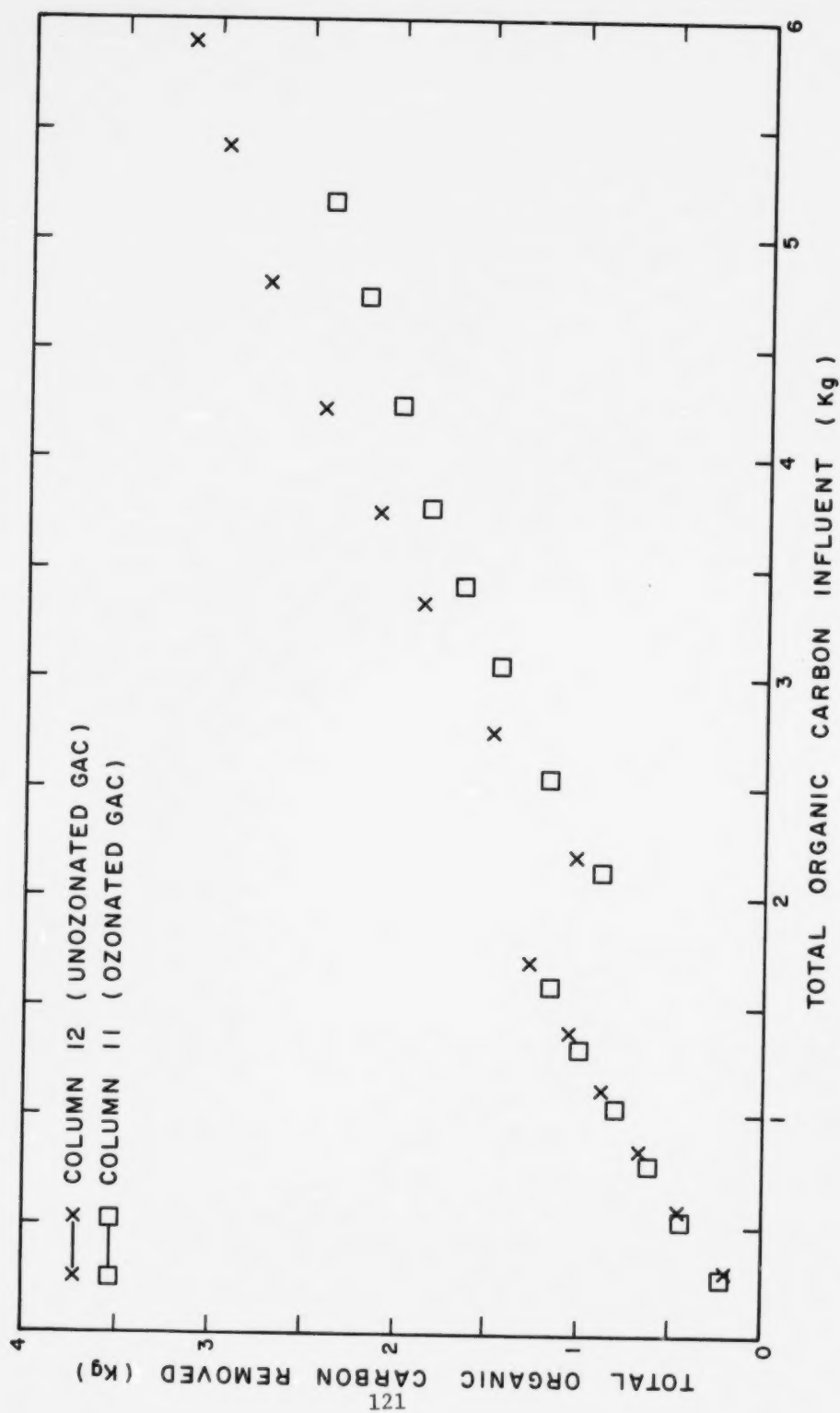


Figure 56. Total Organic Carbon Removed in Phase I-E-2 Study, Columns 12 and 11.

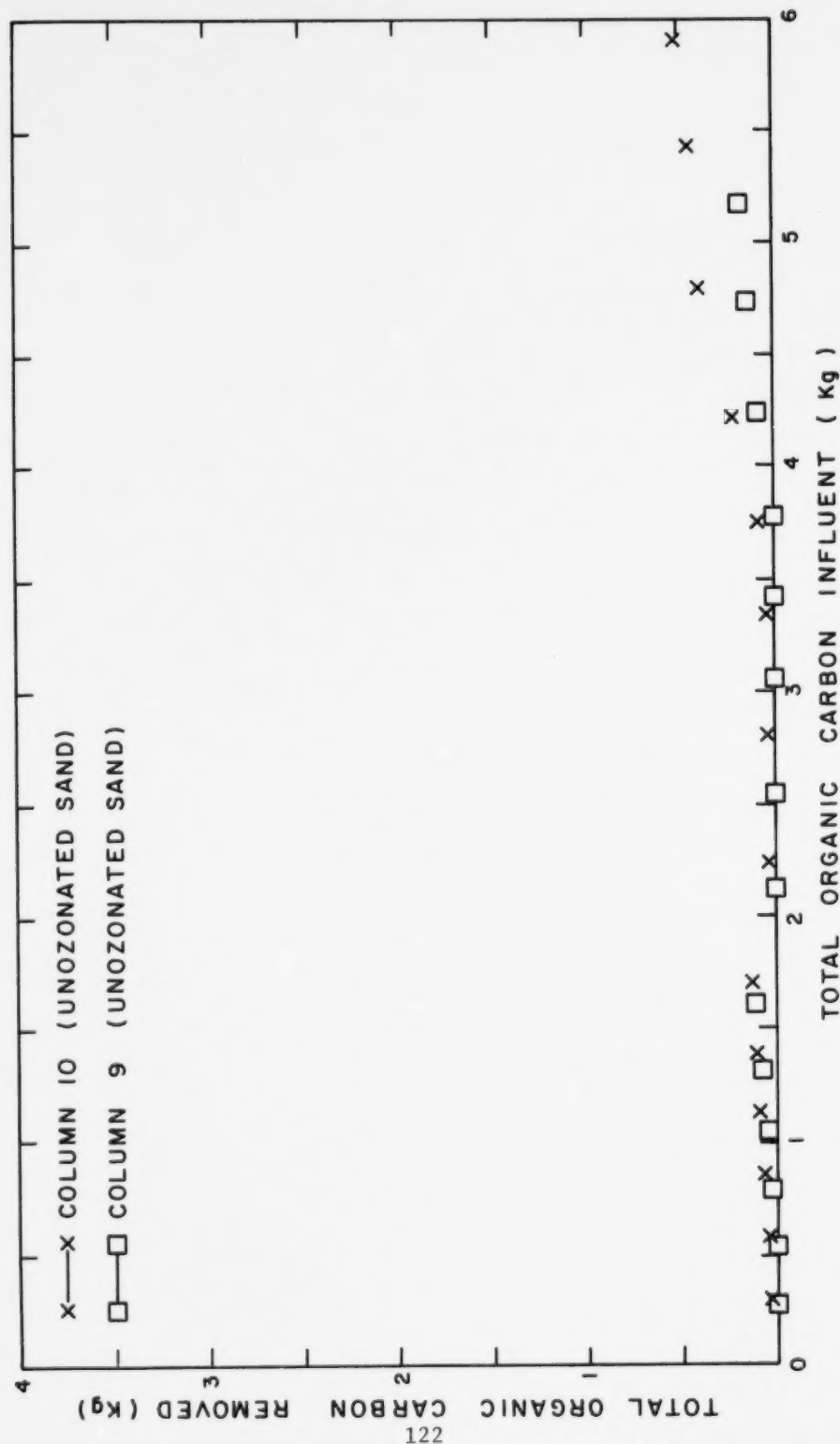


Figure 57. Total Organic Carbon Removed in Phase I-E-2 Study, Columns 10 and 9.

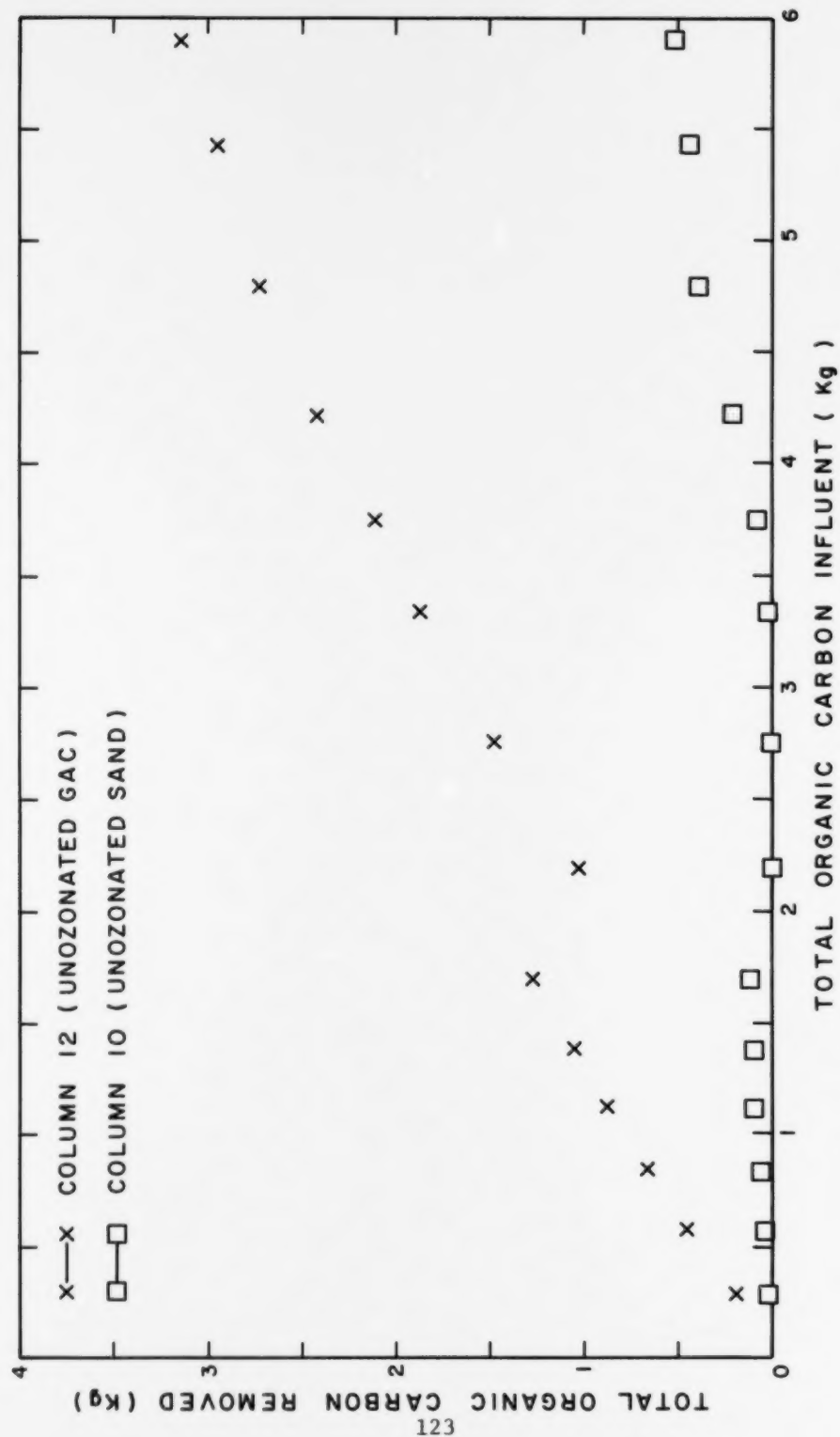


Figure 58. Total Organic Carbon Removed in Phase I-E-2 Study, Columns 12 and 10.

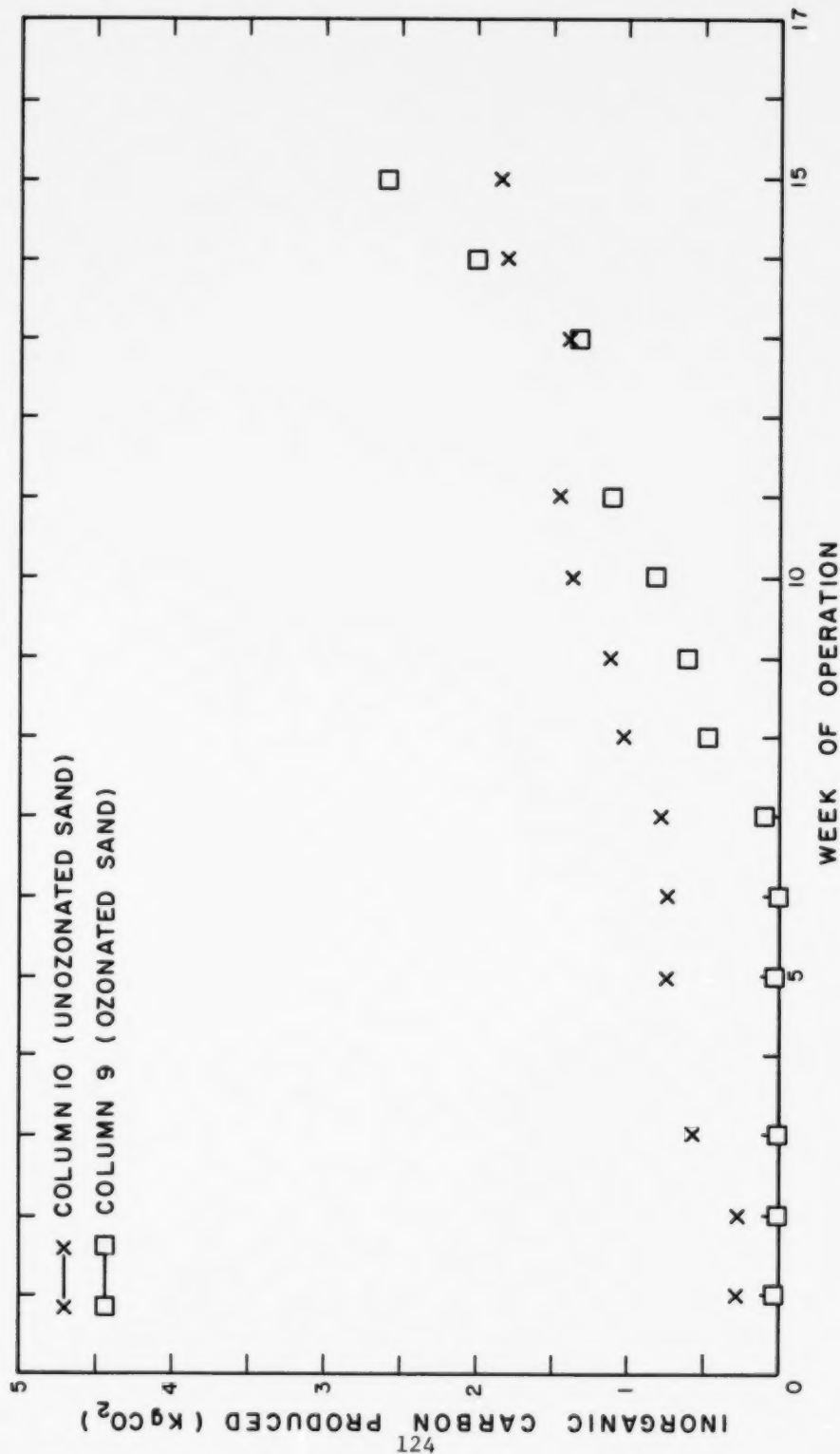


Figure 59. Cumulative Inorganic Carbon Produced in Phase I-E-2 Study, Columns 10 and 9.

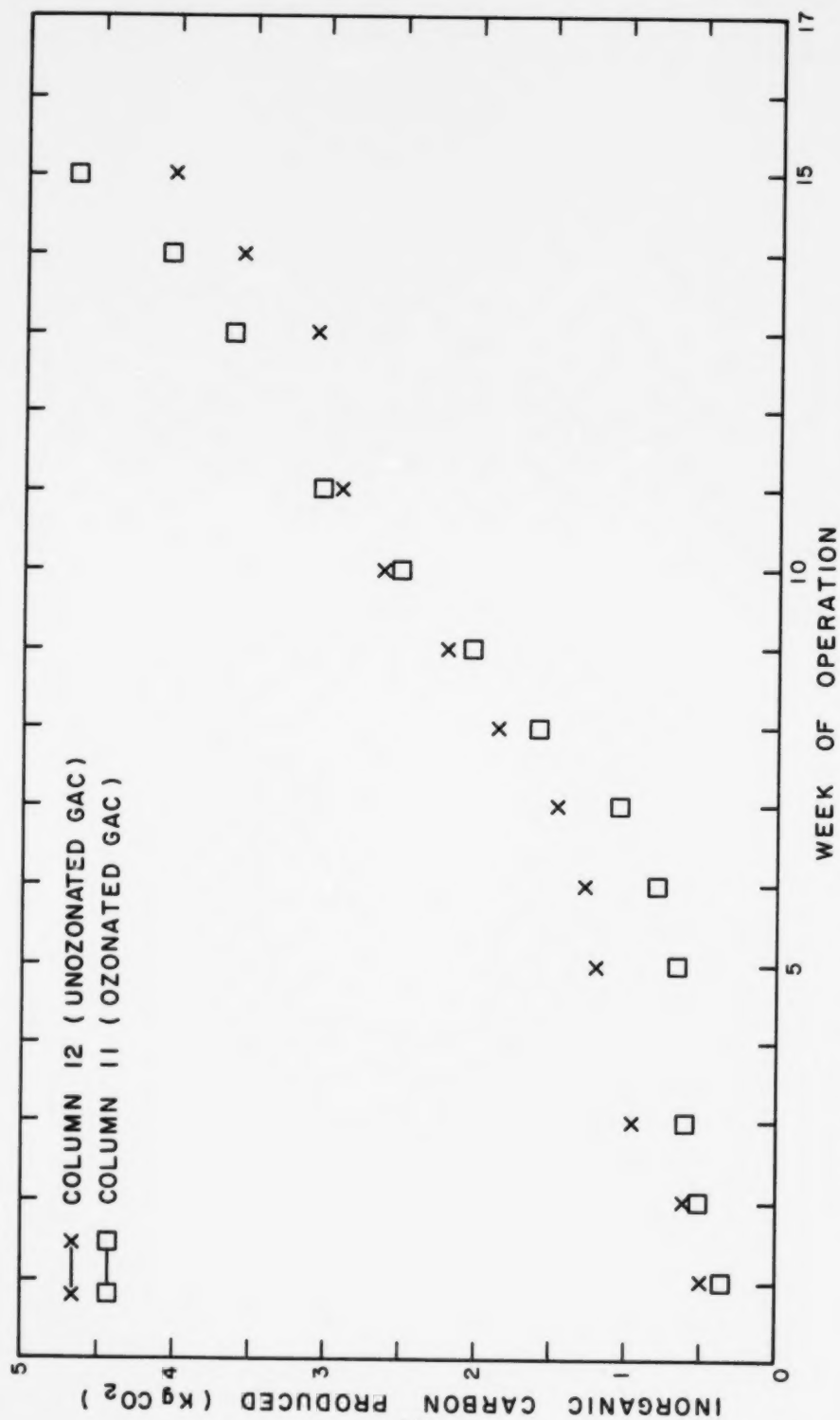


Figure 60. Cumulative Inorganic Carbon Produced in Phase I-E-2 Study, Columns 12 and 11.

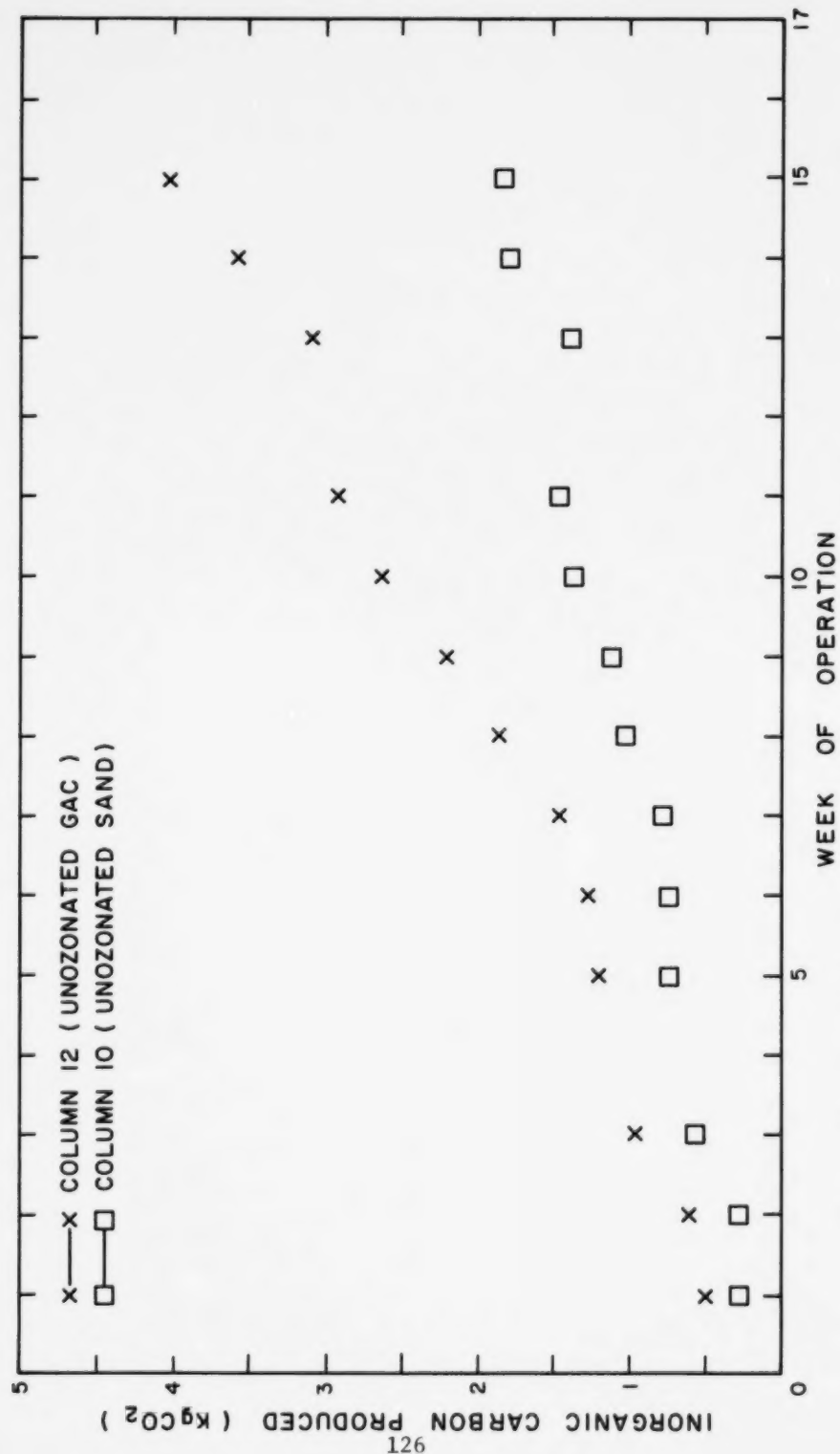


Figure 61. Cumulative Inorganic Carbon Produced in Phase I-E-2 Study, Columns 12 and 10.

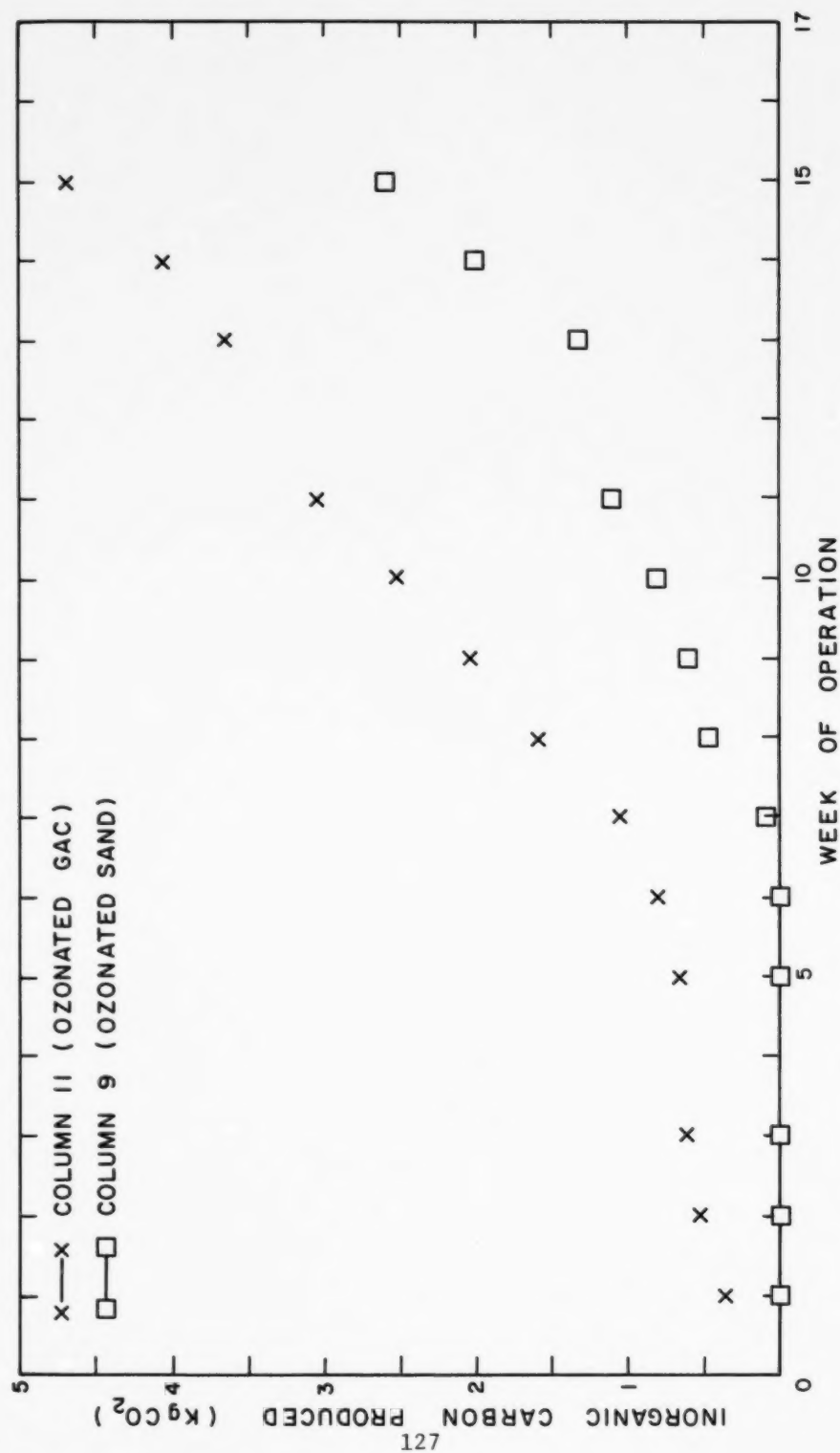


Figure 62. Cumulative Inorganic Carbon Produced in Phase I-E-2 Study, Columns 11 and 9.

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5. TOC removal rates on sand begin also after the twelfth week and are about the same order of magnitude $0.3 - 0.5$ moles TOC/ m^3 -hr. as observed in the GAC column sets 5-6 and 3-4 during the same period (compare Tables 12 and 14). It is not clear why the values are the same, since the modified total plate count and ATP data show that populations are greater on the columns that have been in service for some time. The genera on the older columns may be different, or the sand columns may still be in a phase where macromolecular synthesis is high.

6. Figures 37 - 38 and Table 11 show values of non-purgeable total organic halogen (NPTOX) for several weeks samples taken in Phase I-E-2. NPTOX formation potential values correlate well with THMFP ($r^2 = 0.7$). The ratio of NPTOX to THM produced by chlorination of Cross Lake water is in the range of about two to three.

CONCLUSIONS OF THE PILOT STUDY RELATIVE TO REQUIREMENTS OF THE SAFE DRINKING WATER ACT.

Effective November 29, 1981 cities in the United States with populations above 75,000 must have no more than 0.10 mg/L of the combined THM's in their finished water (17). The City of Shreveport, Louisiana is in this class of cities, and uses water from the same source as the pilot study. Section 8 of this report describes levels of THM's in the city distribution system and in most cases the values are in excess of 0.30 mg/L in the summer and 0.15 mg/L in the winter. Values of this magnitude are not uncommon in plants using high TOC water and free chlorination, especially in the southern parts of the U.S.A. (89). Many of these municipalities will probably consider shifting from free chlorination to chloramination to avoid THM formation. However, free chlorine or an oxidant of equal strength is often required in such plants to control manganese and taste-and-odor problems. Municipalities which choose to convert to chloramination may require an additional oxidant such as permanganate or chlorine dioxide for these purposes. These are costly alternatives to free chlorine, especially for high demand waters. Thus, the addition of granular activated carbon columns in combination with ozone oxidation may be an alternative to be considered, especially if the large costs associated with GAC thermal reactivation can be avoided. The data derived in this project suggest this may indeed be a possibility, depending on the criteria used for reactivation. In the following section these criteria are discussed in the context of a detailed cost analysis of the addition of GAC and O_3 /GAC systems to a filter plant. The results of this analysis suggest that addition of either GAC or O_3 /GAC systems may involve costs which are not unreasonable by current standards.

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TABLE 14. RATE PROCESSES IN SAND AND GAC COLUMNS: PHASE I-E-2

COL. NO.	MEDIUM	OZONE	Moles TOC/m ³ -hr	Moles CO ₂ /m ³ -hr	mMoles THMFP/m ³ -hr
10	SAND	NO	0.48 (a)	0.24 (a')	1.22
9	SAND	YES	0.33 (b)	0.51 (b')	0.71
12	GAC	NO	1.46	0.54	5.7
11	GAC	YES	1.02	0.69	4.6

- (a) Determined during final six weeks of operation; (a') determined during weeks 11-15
- (b) Determined during final six weeks of operation; (b') determined during weeks 12-15

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SECTION 7

ENGINEERING AND COST ANALYSIS

ASSUMPTIONS AND METHODS OF THE COST ANALYSIS

Introduction

The results of the pilot water treatment plant study described in previous sections of this report were analyzed to determine the optimum operating conditions for the removal of TOC and THM precursors at design capacities of 1, 10, and 100 MGD. Four unit processes were considered: ozone generation systems; ozone contact chambers; granular activated carbon (GAC) contactors; and GAC reactivation systems.

Cost estimates for each process were provided by the WATER computer program as described in Estimating Water Treatment Costs by Gumerman, et al. (90). Construction, operation and maintenance (O&M), and total annual costs are presented in both tabular and graphical form with design capacity as the independent variable. Costs are also expressed on a unit capacity basis to illustrate the economies of scale. Various combinations of ozonation and GAC reactivation systems are selected for a biological activated carbon treatment process within an existing conventional water treatment facility.

Design Parameters

Ozonation--

A covered, concrete ozone diffuser chamber provides 10 minutes of contact time between settled and filtered water and the ozone supply. This contact time corresponds to a unit volume of 928 ft.³ per MGD design capacity. The 10-minute contact time is selected as a compromise between the 3-minute contact time and the 40-minute contact and detention time available during the pilot study. It should be recalled that no significant difference in behavior was observed in the pilot study between GAC columns operating with the two ozone contact times, at least during the first 43 weeks of the study when the short contact time was used.

Using the maximum ozone dosage of 2.5 mg/L, a feed rate of 20.9 lbs. of O₃ per day per MGD capacity is obtained. Ozone generators operate with either air (1 MGD) or oxygen produced on-site (10 and 100 MGD) serving as the feed. Power requirements were reported as 11 kwh/lb. O₃ for air systems and 7.5 kwh/lb. O₃ for oxygen systems.

GAC Contactors--

Concrete, gravity GAC contactors are selected because of the higher

costs of steel contactors. For the design capacities considered, 1, 2, and 11 sets of two contactors in series are required. The range of sizes reported by the Gumerman report determines the minimum number of contactors. An overall empty-bed contact time of 25 minutes is selected based on the pilot plant operation. This contact time requires a unit volume of 2,321 ft.³ per MGD capacity.

A hydraulic loading equal to 2.55 gpm/ft.² was maintained during the pilot study. This loading is equivalent to a flow velocity of 0.34 ft./min., a bed depth of 4.25 ft., and a unit surface area of 273 ft.² per MGD capacity. Backwash system O&M costs are calculated by the WATER program using 232 ft.² per MGD capacity (5-ft. bed depth) as an approximation. Capital costs for backwash systems are not included since it is assumed that existing pumping equipment will be utilized.

Costs for the initial charge and makeup quantities of GAC are based on a sliding rate scale as delivered by rail to the site and vary between 67¢ and 87¢ per lb. A bulk density of 29 lbs./ft.³ is used to convert between GAC weight and volume. This density is representative of Filtrasorb GAC manufactured by Calgon Corporation. Hence, approximately 67,300 lbs. of GAC per MGD capacity are required for plant start-up. If on-site reactivation is desired, a second charge of GAC will be necessary for batch operation of the treatment process.

Costs for a GAC reactivation service are considered as an alternative to on-site reactivation at low design capacities. Spent GAC would be replaced by virgin GAC at a discount rate of 54¢ per lb. as quoted by Calgon Corporation. A replacement facility is assumed to be available within a 100-mile radius.

GAC Reactivation--

The minimum breakthrough period observed during the pilot tests was 24 weeks. Breakthrough is defined according to two criteria as reported in Interim Treatment Guide for Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon (40). The first guideline requires a minimum TOC removal efficiency of 50 percent. This minimum was reached after 24 weeks of operation. The second criterion establishes the maximum terminal-THM effluent concentration of 0.10 mg/L. This maximum was achieved after 52 weeks. Therefore, both 24-week and 52-week reactivation cycles are considered. These cycles produce reactivation rates of 401 and 185 lbs./day per MGD capacity, respectively. A loss factor of 10 percent is selected as being a conservative estimate for the various GAC reactivation techniques. The makeup supply rates for the given reactivation rates equal 18.5 and 40.1 lbs./day per MGD capacity.

Spent GAC is reactivated on-site by either multiple hearth furnaces (10 MGD/52 weeks) or fluidized bed furnaces (10 MGD/24 weeks and 100 MGD/24 and 52 weeks). At the higher capacities, O&M costs for the fluidized bed furnaces are significantly less than those for multiple hearth furnaces while construction costs remain about equal. Due to the batch operation of the GAC contactors, elevated steel-plated GAC storage and/or dewatering tanks are necessary both before and after the reactivation process. At the 1 MGD

design capacity, it becomes more economical to purchase virgin GAC from a reactivation service rather than to reactivate on-site.

Capital and Unit Cost Factors

Capital Cost Factors--

All sitework and interface piping costs equal 5 percent of process construction costs. General contractor overhead and profit vary between 8.5 percent and 12 percent of construction plus sitework costs. Engineering fees are estimated at 10 percent of construction, sitework, overhead, and profit. Legal, fiscal, and administrative costs and interest owed during construction are added to determine the total capital expenditure. Capital costs are amortized over 20 years at 10 percent interest. This interest rate was the maximum rate considered by the Gumerman report and is the basis for the interest during construction estimate. Capital costs are combined with O&M costs to produce total annual costs in both dollars and cents per thousand gallons.

Land, subsurface, and standby power requirements are neglected since construction would occur at an existing treatment facility. All construction costs are updated by the Winter 1980 ENR Construction Cost Index (CCI). This represents almost a 19 percent increase over the costs reported by Gumerman, et al. in October, 1978 (CCI = 315 vs. 265.)

Unit Cost Factors--

A summary of pertinent unit prices associated with O&M costs are listed below.

TABLE 15. UNIT COST FACTORS

Category	Unit	Cost Factor
Electricity	\$/kwh	0.05
Labor	\$/hr	15.00
Natural Gas	\$/1,000 scf	3.70
Diesel Fuel	\$/gal	1.00
Building Energy Use	\$/ft. ² /yr.	5.13

RESULTS AND DISCUSSION

Unit Processes

Construction and O&M costs for each unit process are listed in Tables 16, 17 and 18. It is apparent that such items of construction as bulk purchase of GAC and the associated storage and dewatering vessels do not experience the same economies of scale as the remaining processes. There-

TABLE 16. CONSTRUCTION COSTS FOR VARIOUS UNIT PROCESSES

System	Design Capacity (MGD)		
	1	10	100
Ozone Generating System \$	92,700	\$ 451,000	\$1,820,000
Ozone Contact Chamber	10,100	49,300	240,000
GAC-Initial Charge (ea.)	49,700	483,000	4,480,000
Concrete Gravity GAC Contactors	294,000	1,060,000	7,580,000
Multiple Hearth Furnace- 24-Week Cycle	---	---	---
52-Week Cycle	---	780,000	---
Fluidized Bed Furnace- 24-Week	---	1,040,000	1,730,000
52-Week	---	---	1,420,000
GAC Storage and Dewatering Tanks	51,300	430,000	4,240,000

TABLE 17. O&M COSTS FOR VARIOUS UNIT PROCESSES (IN DOLLARS PER YEAR)

System	Design Capacity (MGD)		
	1	10	100
Ozone Generating System	\$ 14,200	\$ 51,400	\$ 333,000
Concrete Gravity GAC Contactors	20,000	68,900	415,000
Makeup GAC-24 Week Cycle	79,000*	115,000	1,130,000
52 Week Cycle	36,300*	55,100	524,000
Multiple Hearth Furnace- 24 Week Cycle	---	---	---
52 Week Cycle	---	68,600	---
Fluidized Bed Furnace- 24 Week Cycle	---	70,500	290,000
52 Week Cycle	---	---	180,000

*Carbon Reactivation Service

TABLE 18. O&M COSTS FOR VARIOUS UNIT PROCESSES (IN CENTS PER THOUSAND GALLONS)

System	Design Capacity (MGD)		
	1	10	100
Ozone Generating System	3.9	1.4	0.9
Concrete Gravity GAC Contactors	5.5	1.9	1.1
Makeup GAC-24 Week Cycle	21.6*	3.2	3.1
52 Week Cycle	10.0*	1.5	1.4
Multiple Hearth Furnace-24 Week Cycle	---	---	---
52 Week Cycle	---	1.9	---
Fluidized Bed Furnace-24 Week Cycle	---	1.9	0.8
52 Week Cycle	---	---	0.5

*Carbon Reactivation Service

fore, these items command a larger portion of the total construction cost at higher design capacities.

Ozonation costs, however, diminish in importance at higher capacities. This is also true of fluidized bed furnaces which exhibit a very flat construction cost curve over the operating range.

O&M costs per thousand gallons treated at 1 MGD are four to seven times those calculated at 100 MGD, indicating significant economies of scale. Relative to the volume of water treated, GAC makeup and reactivation represent the dominant cost items, ranging from 50 to 70 percent of the total O&M cost.

Combined Systems

Table 19 presents annual costs for various combinations of unit processes which could conceivably be employed in the modification to an existing water treatment plant. Reactivation cycles of 24-weeks and 52-weeks were considered along with the "no reactivation" alternative. These annual costs are plotted in Figures 63 and 65 in total dollars and cents per 1000 gallons respectively, for cases in which 25 minutes EBCT of GAC is added to existing plants of 1, 10 and 100 MGD capacity. Figures 64 and 66 are similar representations for the O₃/GAC system.

Figures 67 and 68 present the cost data in a manner which emphasizes the effect of reactivation frequency on annual costs. The dotted lines refer to costs with no regeneration, i.e. with infinite time between reactivation. While this is probably an unrealistic scenario, it represents the limit of cost lowering which can be achieved as the time between reactivations may be increased.

CONCLUSIONS

There are several conclusions which are appropriate to make from the cost data included in the foregoing tables and figures. First, the data in Table 19 show that amortized capital comprises between 40 and 80 percent of the total annual cost. This fact is indicative of the capital intensive nature of GAC treatment processes in general. Energy and material intensive processes such as ozone production and GAC reactivation reduce the capital cost fraction of the overall total. Lower design capacities also reduce the percentage of total annual costs due to capital investment.

Second, Figures 67 and 68 illustrate the benefits to be accrued by extending the time between GAC activations. The effect is more pronounced for small plants, but even at 100 MGD extension of the reactivation interval from 24 to 52 weeks results in an overall saving of 2¢ per 1000 gallons. The pilot plant data discussed in Section 6 demonstrate that such a savings is entirely feasible, and, indeed, proper management of the microbiological activity on GAC columns may allow one to increase the reactivation interval even further.

Third, it is clear from table 19 that ozonation at approximately

TABLE 19. ANNUAL COST FOR VARIOUS COMBINATIONS OF UNIT PROCESSES

Unit Process Combination	ANNUAL COSTS (\$)			ANNUAL COSTS (¢/KG)		
	Design Capacity (MGD)			Design Capacity (MGD)		
	1	10	100	1	10	100
Ozonation Only	\$ 30,800	\$ 133,000	\$ 675,000	8.4	3.6	1.8
GAC Only-24 Week Cycle	165,000	825,000	5,690,000	45.1	22.6	15.6
52 Week Cycle	121,000	723,000	4,930,000	33.2	19.8	13.5
No Reactivation	75,600	319,000	2,420,000	20.7	8.8	6.6
Ozonation/GAC-24 Week Cycle	195,000	960,000	6,350,000	53.5	26.3	17.4
52 Week Cycle	152,000	854,000	5,620,000	41.7	23.4	15.4
No Reactivation	115,000	522,000	3,800,000	31.5	14.3	10.4

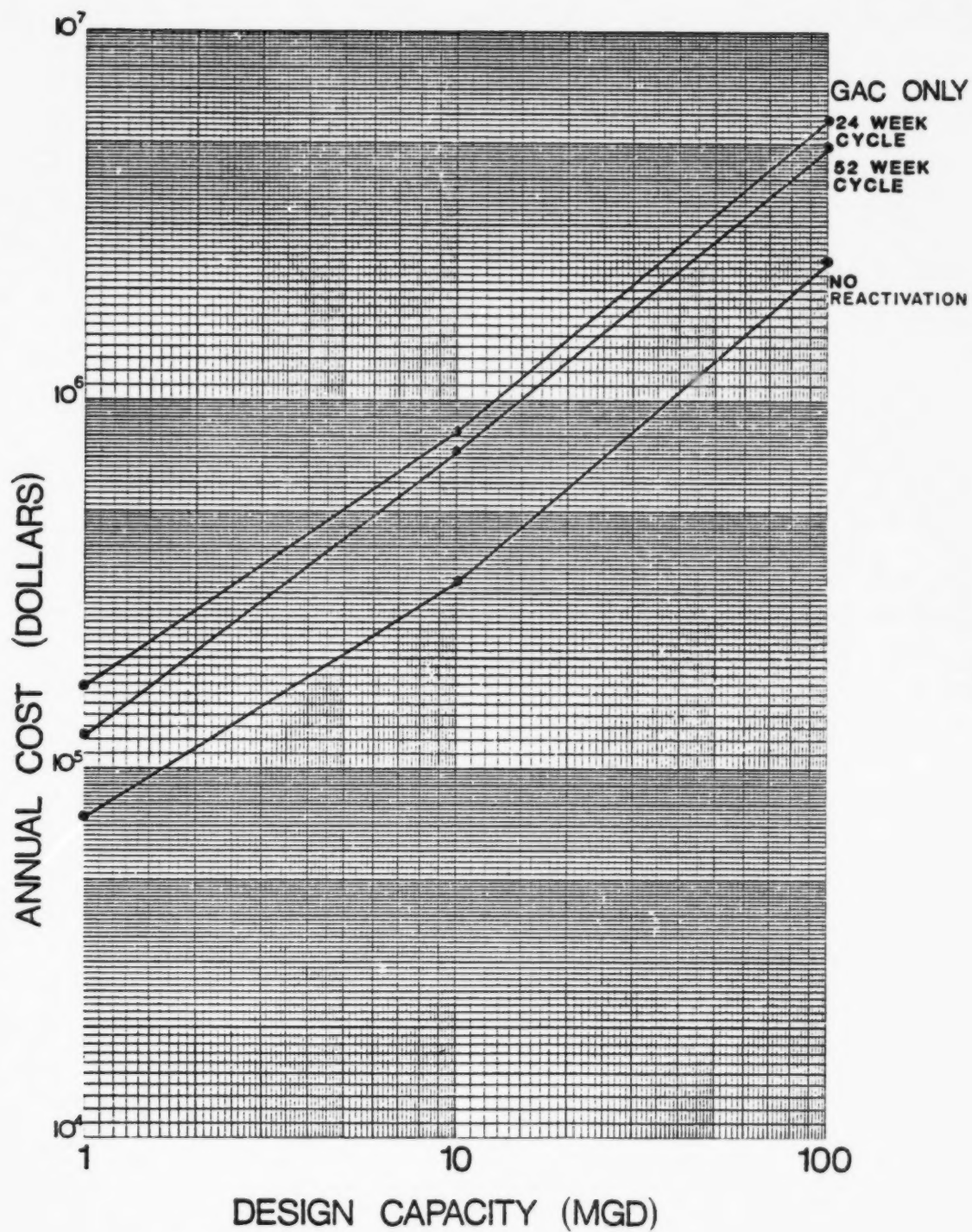


Figure 63. Annual Cost for GAC Treatment.

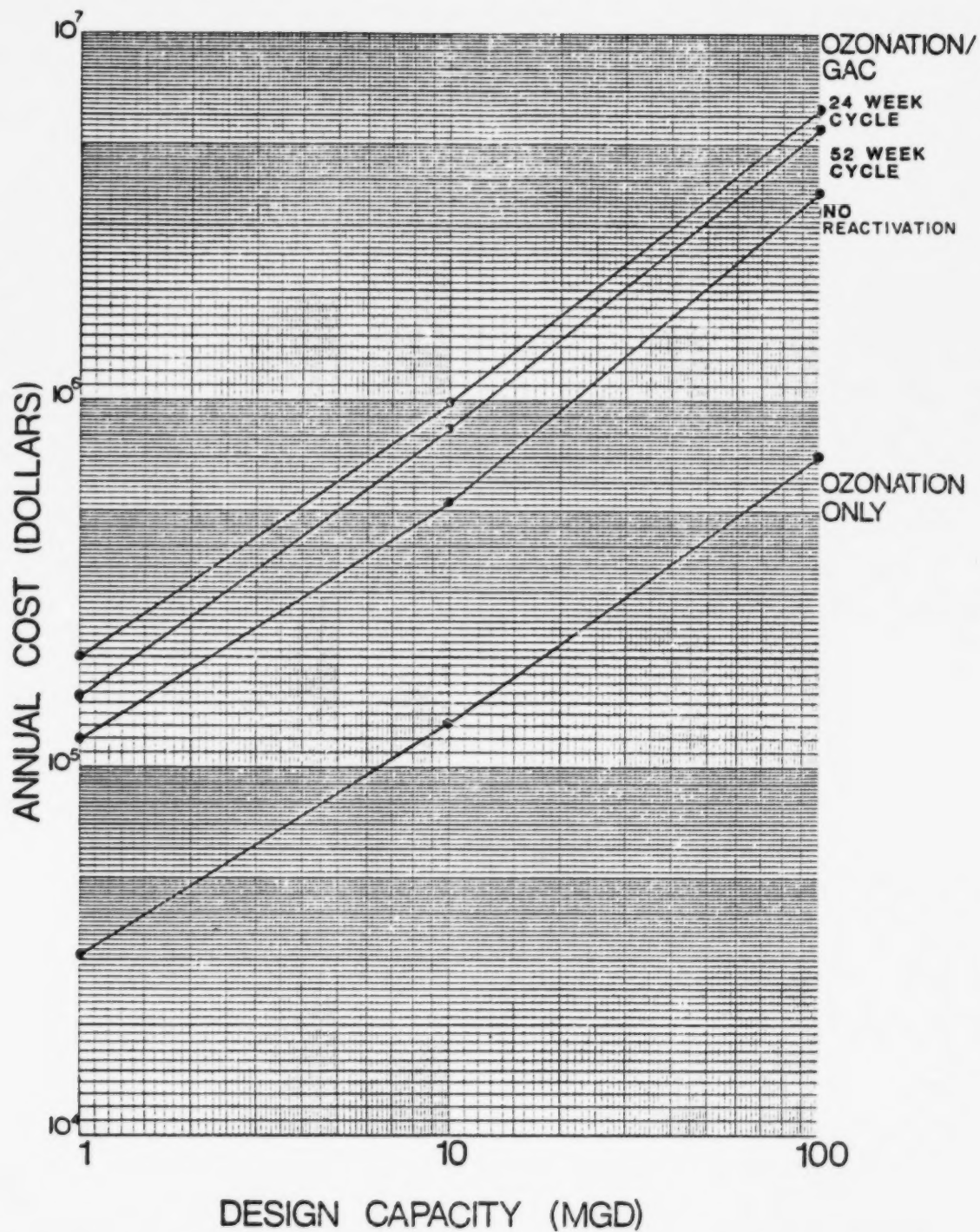


Figure 64. Annual Cost for Ozonation in Combination with GAC Treatment.

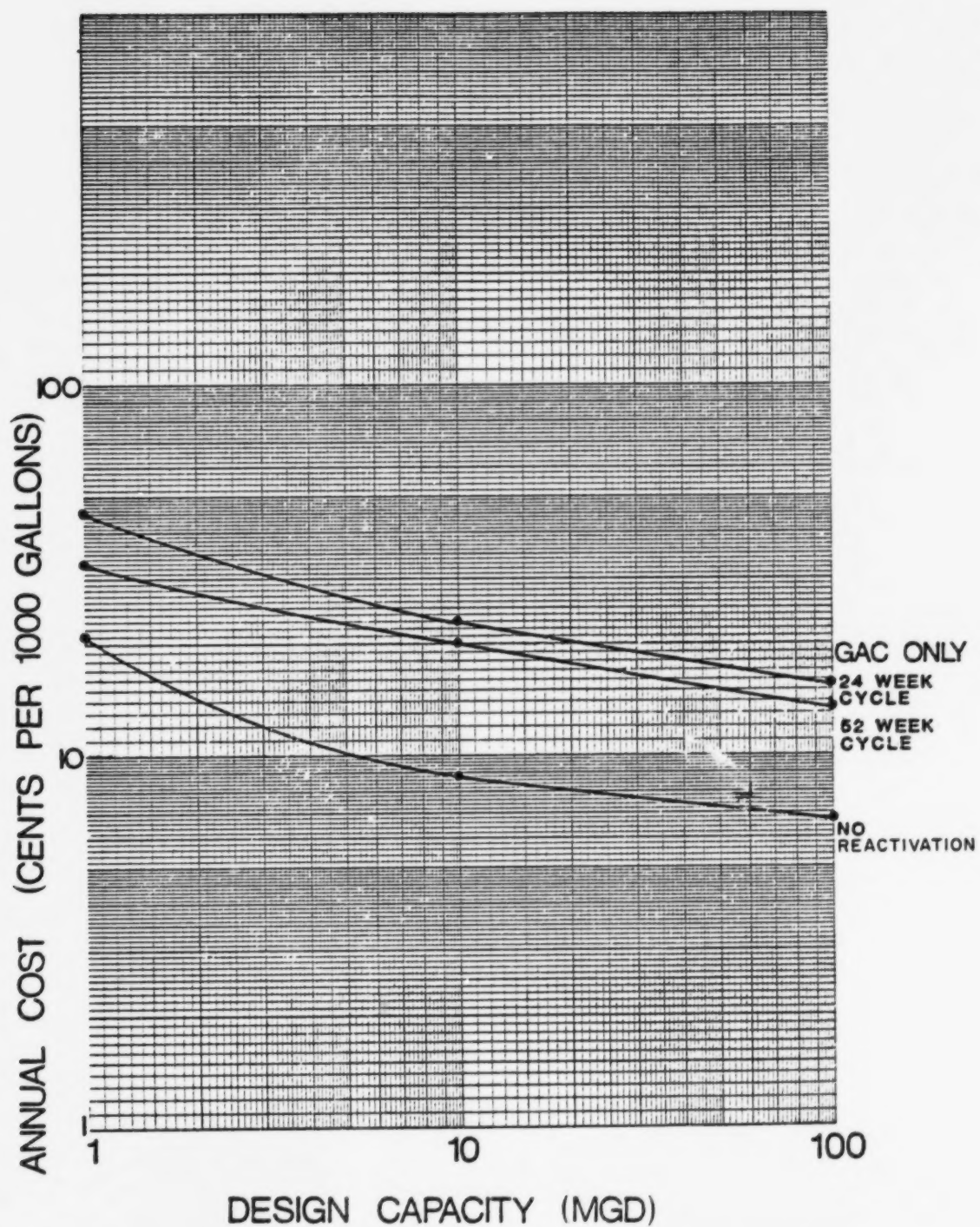


Figure 65. Annual Cost per Thousand Gallons for GAC Treatment.

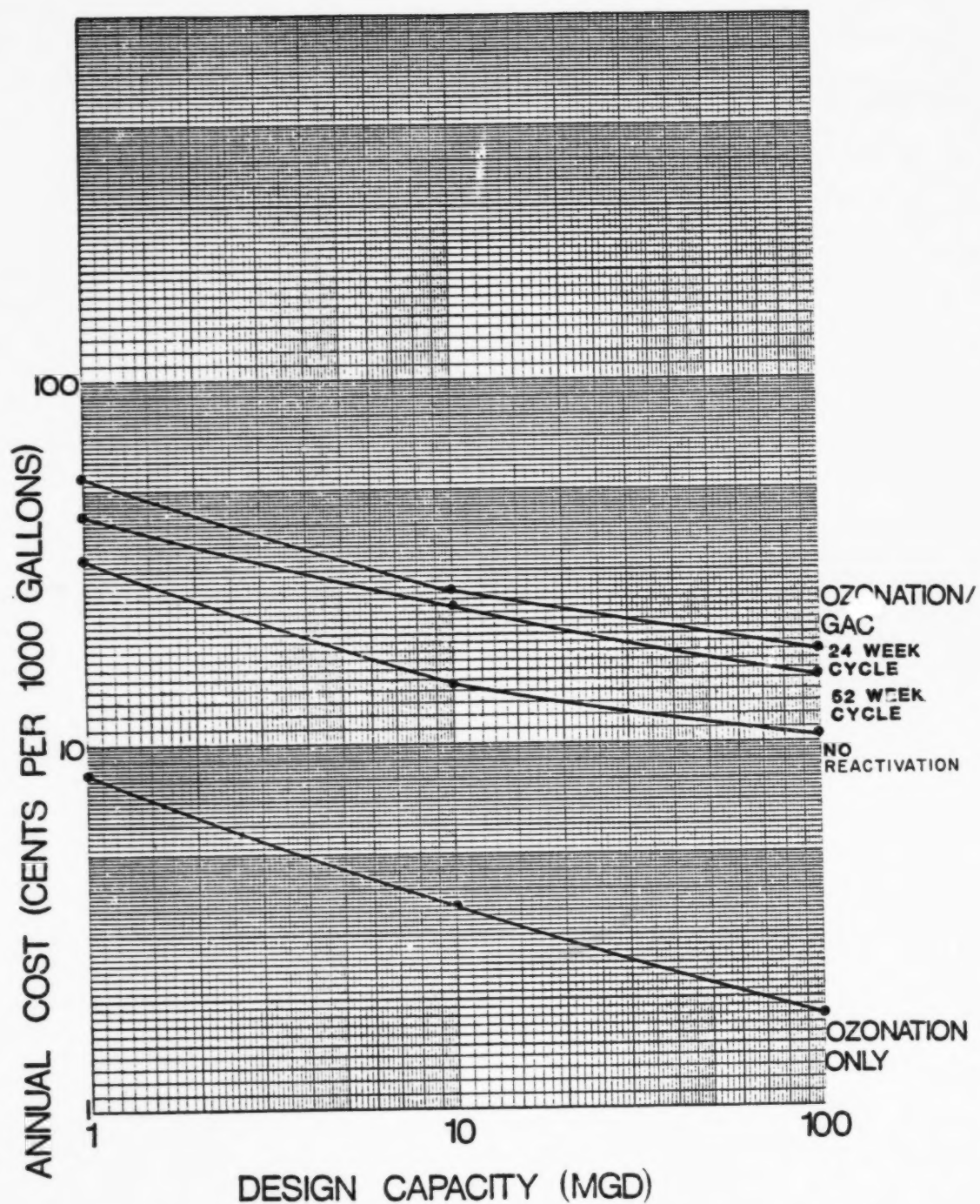


Figure 66. Annual Cost per Thousand Gallons for Ozonation in Combination with GAC Treatment.

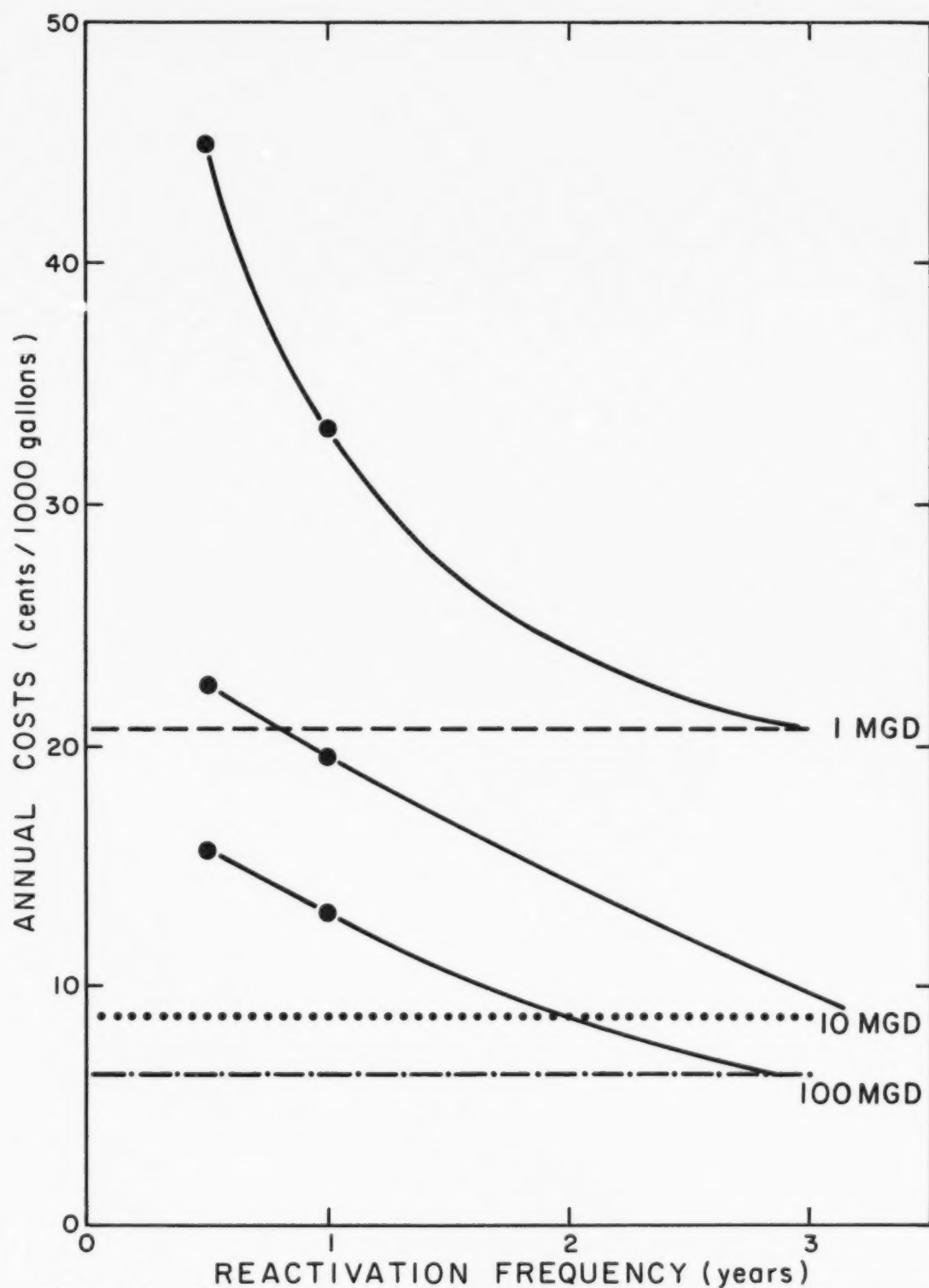


Figure 67. Effect of Plant Size on Range of Annual Costs for Addition of GAC with Various Reactivation Frequencies.

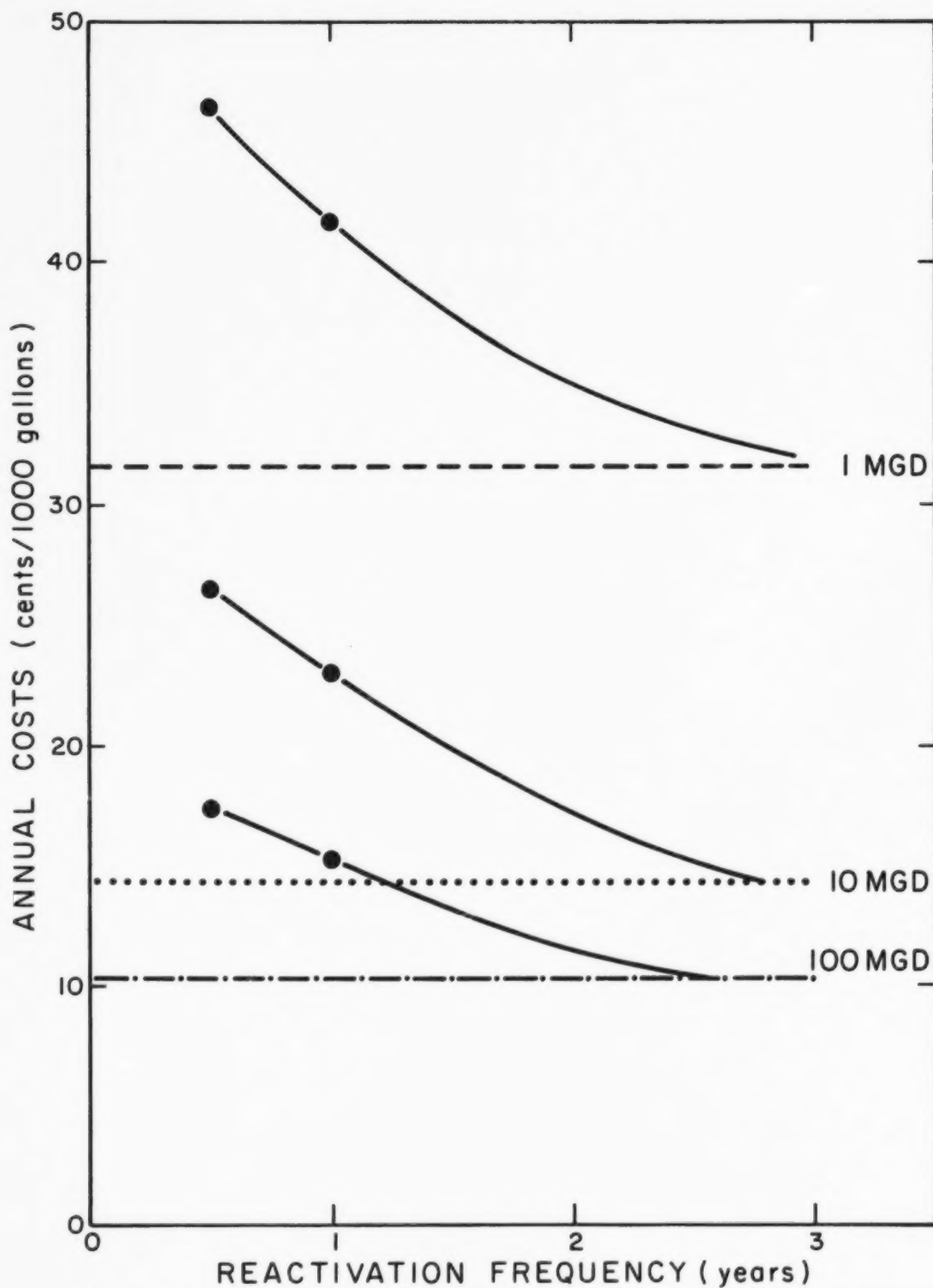


Figure 68. Effect of Plant Size on Range of Annual Costs for Addition of O_3 /GAC with Various Reactivation Frequencies.

2.5 mg/L adds substantially to the cost of the GAC treatment train. (At a 52 week reactivation cycle ozone adds from 13 to 25% additional costs for 1, 10 and 100 MGD plants). Higher doses of ozone would be even more expensive. Gumerman et al. (90) have shown that costs for increased ozone capacity are approximately linear in the range of interest here, i.e. doubling the ozone dose will almost double the O&M and ozone generator costs. Thus, ozonation must provide some benefit to offset these increased costs. As noted in Section 6, it is not clear from the pilot study on Cross Lake that ozonation has provided substantially increased operating efficiencies of the GAC columns. The data in Section 6 show at best that ozone increases the lifetime of GAC columns from approximately 52 weeks to approximately 65 weeks*. For the most favorable case, the 100 MGD plant, this would correspond to annual costs of 13.5¢/Kg for the GAC system and 14.2¢/Kg for the O₃/GAC (Table 20). In other words, the addition of ozone is not cost effective. Put another way, in order to be cost effective, GAC reactivation time for the O₃/GAC system would have to be extended to approximately 2.2 years for 1 MGD, 1.5 years for 10 MGD, and 1.3 years for 100 MGD plants (Table 20, far right-hand column). Although the European experience has been interpreted by some to indicate that such service times are possible, the data from this project do not allow such a conclusion.

Finally, it is possible that longer reactivation cycles may be accomplished with higher ozone doses and more efficient management of the microbiological processes which occur on GAC columns. More importantly, while the addition of ozone may be marginally cost effective for THM precursor control, it should also be recognized that ozonation may cause other savings by the elimination of the need for another preoxidant. Preoxidation will almost certainly be required in many southern U.S. plants such as Shreveport for taste and odor control and for removal of excess manganese. For such purposes, prechloramination is not a viable alternative, although it will successfully control THM production. Therefore, it is conceivable that combinations of ozonation and GAC filtration may prove to be the most cost effective alternative for the control of THM's and for the other purposes noted above.

TABLE 20. ANNUAL COSTS FOR GAC AND O₃/GAC SYSTEMS WITHOUT EXCEEDING THE 0.10 MG/L THMFP CRITERION (¢/KG)

Design Capacity	GAC (52 weeks)	-----O ₃ /GAC*----- (65 weeks)	Weeks to equal GAC only
1 MGD	33.2	39.7	2.2
10 MGD	19.8	21.2	1.5
100 MGD	13.5	14.2	1.3

* Data interpolated from Figures 67 and 68

*Using the 0.10 mg/L THMFP criterion.

SECTION 8

FULL SCALE PLANT MODIFICATION ALTERNATIVES FOR CONTROL OF TRIHALOMETHANES

DESCRIPTION OF SHREVEPORT WATER TREATMENT FACILITIES

The City of Shreveport is served by two separate water treatment facilities, the McNeil Street plant and the T.L. Amiss complex, both of which receive Cross Lake water. The McNeil Street plant is located in and serves the downtown area. Phase II of the project primarily involved the T.L. Amiss complex, located on Cross Lake, and the area that it serves. The T.L. Amiss complex consists of two independent plants which share a common clearwell. Plant I was built in 1936 with additions made in recent years; the smaller Plant II was completed in 1968.

Plant II

The inlet for Plant II is located 500 ft. from the shore in 10 ft. of water. Prechlorination occurs at the intake crib. A 60" line leads to the low service pumping station on the shore. After a brief retention time in a reservoir at the pump house, the water is then pumped 830 ft. to a Parshall flume as shown in Figure 69. Dissolved alum is dripped onto the raw water at the point of most rapid mixing in the flume. The water then flows by gravity to three sets of slow mix and settling basins in parallel. Each slow mix basin is a 27 ft. long chamber divided in half by a wooden baffle wall. Each half is stirred by a ten ft. dia. horizontal paddlewheel to aid flocculation. The flocculated water from the slow mix basin then flows through another baffle wall into a 60' x 60' settling basin with a circular bottom scraper. The settled water then passes through a baffle wall into another 60' x 60' basin. This basin has overflow weirs across the back half. The water from the three sets of weirs is combined and goes to a 180' x 30' stabilization basin. Lime is added to the water in a short flume in the stabilization basin. The water is chlorinated a second time before flowing into one of four 37' x 30' filter basins containing 40" of filter media. The media consists of 8" Anthra-filt, 1'-8" sand, 4" coarse sand, and 10" gravel supported by 10-1/2" filter blocks. The filtered water is chlorinated a third time as it flows to a 5 million gallon clearwell shared with Plant I. Refer to Table 21 for capacities and retention times at 12 MGD of Plant II.

Plant I

Plant I has a treatment process basically the same as Plant II.

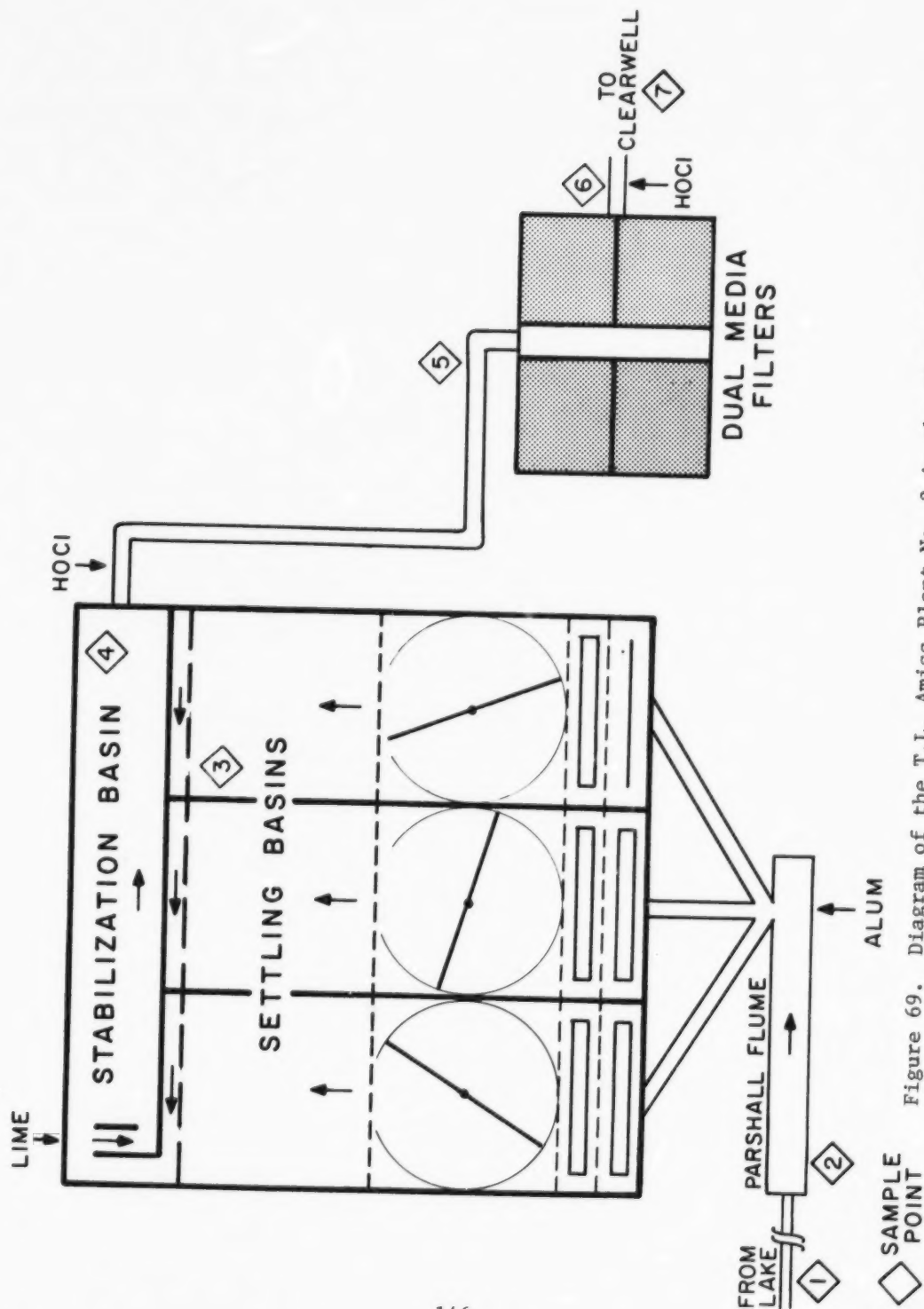


Figure 69. Diagram of the T.L. Amiss Plant No. 2 in the City of Shreveport, Louisiana. Prechlorination at the Lake Intake.

TABLE 21. COMPONENTS OF PLANT II, T. L. AMISS COMPLEX, SHREVEPORT, LA.

	Sample Point	Capacity in 1000 gal.	Retention time in hrs. at 12 MGD	Cumulative Retention Time
Lake	1			
Intake line		73	.15	.15
Pumping station		133	.27	.42
Raw water line	2	77	.15	.57
3 slow mix basins		442	.88	1.45
3 1st settling basins		1,050	2.1	3.55
3 2nd settling basins	3	1,050	2.1	5.65
Stabilization basin	4	403	.81	6.46
4 filters	5 & 6	<u>300</u>	<u>.60</u>	7.06
		3,528	7.06	
Clearwell	7	5,000		

Plant I is normally operated continuously at up to 36 MGD depending on distribution system demand. Plant II is operated when needed to supplement Plant I. The combined maximum output for both plants is about 60 MGD.

SUMMARY OF THM LEVELS IN SHREVEPORT DISTRIBUTION SYSTEM

Since Shreveport's water source, Cross Lake, is high in natural organics the formation of trihalomethanes is unavoidable when a free chlorine residual is maintained. As shown in the 1980 data in Figure 70, THM's are first formed upon chlorination and continue to be formed throughout the treatment process and distribution system. The top line indicates the raw water formation potential which is probably the maximum possible THM value attainable.

As can be seen from Figure 70, THM values are significantly lower in the winter of 1980 than in the summer. Since the raw water THM formation potential value, which is found at a constant temperature is correspondingly lower in the winter the lower values are probably due to a change in the nature of the organics in the water from season to season.

Figure 71 shows plots of Inst TTHM values at three points in the city's distribution system during the period 1980-81. The three points, which receive exclusively T.L. Amiss plant water, are spread through the city with Greenwood Road closest to the plant, E. 70th at about twice that distance, and Lucas at the end of the system on a dead end line. As can be seen from the plots, water high in THM is delivered to the consumer throughout the year. Obviously THM reduction must be accomplished in order to meet the requirements of the National Interim Primary Drinking Water Standards.

THM CONTROL ALTERNATIVE STUDIES

A major objective of this project was to determine if THM levels leaving Amiss Plant No. 2 could be lowered by in-plant operational changes. Based on results of some preliminary monitoring of Plant No. 2, several full-scale experiments were planned to examine the effect of treatment modifications.

Two basic points governed any actions to be taken:

1. Public health protection must be maintained and documented, and
2. Treatment modifications were restricted or bounded by characteristics of the treatment plant; i.e. points and sequence of chemical addition, mixing effectiveness, reaction time available and once-through contact with reagents.

The following approaches were considered:

1. Decrease THM formation by lowering finished water pH, or by elimination of predisinfection,
2. Removal of THM precursors with powdered activated carbon (PAC) or polymer,

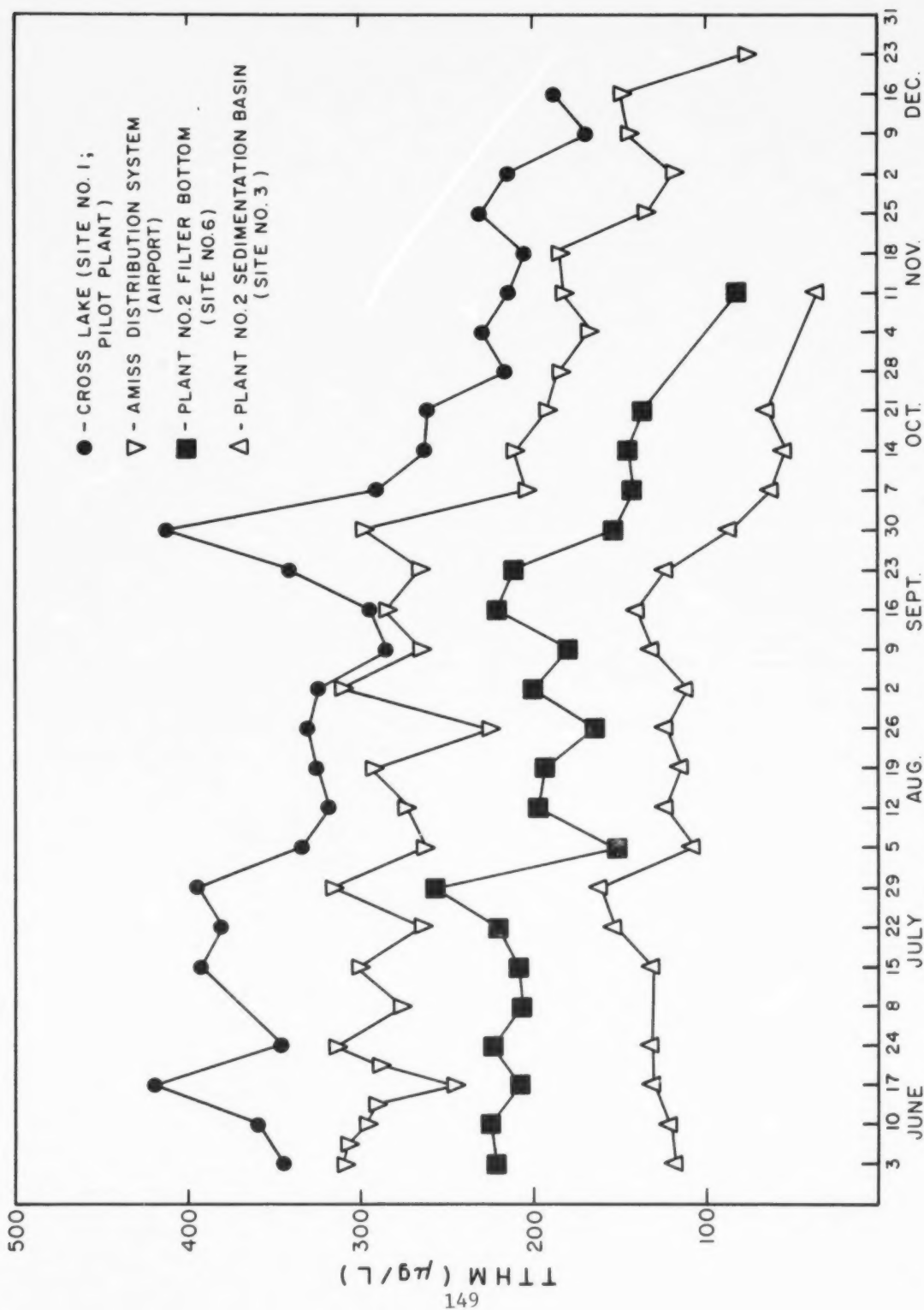


Figure 70. Inst TTHM Values in the Amiss Plant No. 2 and at the Airport Sampling Point in the Distribution System. Values at Site No. 1 are THMFP Values Using 20 mg/L HOCl dose at pH 6.5 with 3 Day Detention.

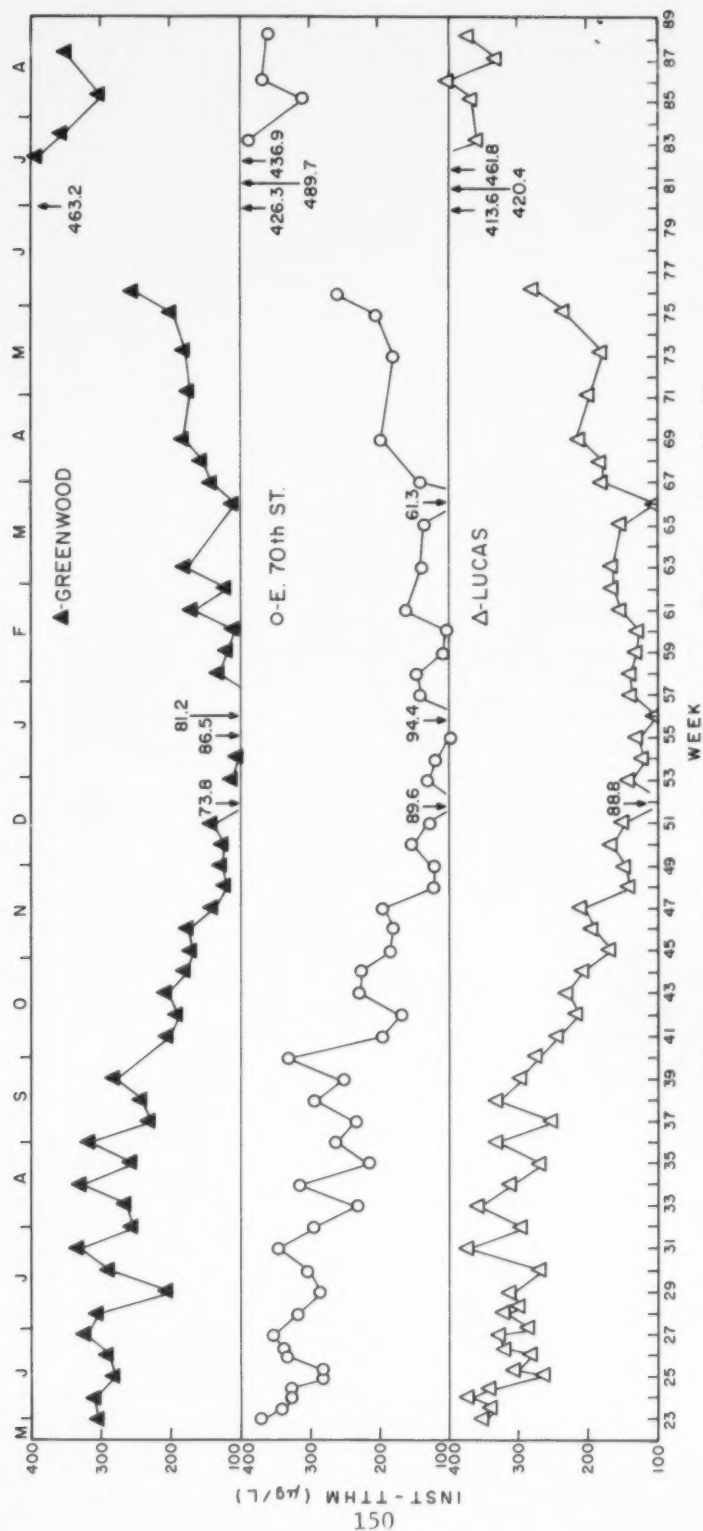


Figure 71. Instantaneous TTHM values at Three Points in the Shreveport Distribution System. Week numbers refer to Operational Period of Pilot Plant, 1980-81.

3. Remove THM formed by pre and/or secondary (post flocculation, prefiltration) chlorination, with granular activated carbon (GAC) or polymer, and
4. Elimination of prechlorination and substitution of an alternative disinfectant such as chlorine dioxide or chloramines.

Plant Modification Tests

Plant scale tests were initiated based on the previously outlined approaches and on the constraints noted earlier.

During the period October 5, 1979 - November 5, 1979 an experiment was carried out in cooperation with plant personnel at the Amiss Treatment Plant in Shreveport, the purpose of which was to determine if THM's levels leaving the Amiss plant No. 2 could be effected by one of three approaches:

- a) decreasing the chlorine dose at the raw water intake pump (prechlorination)
- b) lowering the pH of the water leaving the lime stabilization basin from ca. 9.3 to 8.8
- c) elimination of prechlorination in conjunction with an increase in alum feed.

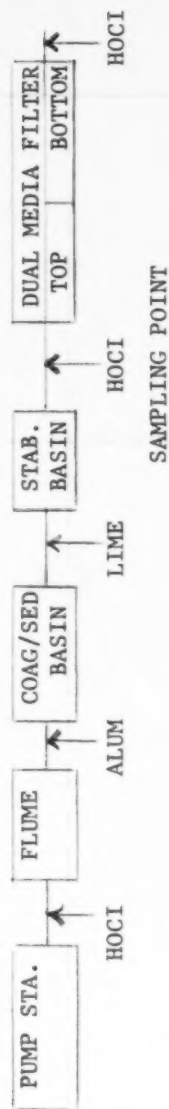
Following preliminary examination of the data, experiment c (above) was continued during a two-week period from November 30 - December 10, 1979.

The duration of the initial experiment consisted of four weeks, each of which involved the change of one or two operational parameters in the Amiss plant No. 2. Conditions during the four week period are shown in Table 22. It is seen that during week one the plant was operating in the "normal" mode for the season, with a prechlorine dose of 7.4-7.6 mg/L resulting in a residual at the flume (Site 2) of 1.0-3.0 mg/L. At the end of the week chlorine residual was high presumably due to a cool weather front that moved through the area. Alum and lime feed rates averaged 44 and 22 mg/L respectively during this period. During the second week two parameters were changed. The pH target was lowered to 8.5 and the chlorine dose was lowered to 5.3-5.5 mg/L. However, the residual at Site 2 remained high 1.7-2.0 mg/L. Lime and alum feed rates were approximately the same. Chlorine demand during week 1 was about twice as large as during week 2.

In week three the pH target was raised to 9.2, keeping the prechlorine and alum doses constant. Thus, weeks two and three comprise an experiment in which only one parameter (pH) was changed, although it must be conceded that the pH control during the two weeks left much to be desired.

In week four the prechlorine dose was removed, but there remained a small residual in the reservoir between the pump station and the flume (site 2). Chlorine dose between sites 4 and 5 was increased so as to maintain a good residual at the filters. Prechlorination was also discontinued prior to week 5 and none was used through week 6.

TABLE 22. OPERATING PARAMETERS AT THE T. L. AMISS PLANT DURING pH AND CHLORINE CONTROL EXPERIMENTS



PLANT NO. 1														
PLANT NO. 2														
DATE (1979)	pH			Free residual Chlorine (mg/L)			Chemical feed rate			Filter Effluent		Cl Feed		
	2	5	6	2	5	6	Alum (mg/L)	Lime (mg/L)	Chlorine pump sta.	(mg/L) Site 4-5	pH	Cl Res.	a	b
10-5	6.7	9.4	9.1	3.0	3.0	3.0	43	20	7.4	1.0	9.0	1.3		
6		9.5	9.0						7.5	1.1	9.0	1.5	7.7	0.4
7	6.4	7.4	8.3	2.5	2.0	2.0	44	24	7.5	1.1	9.0	2.0		
8		8.5	8.8						7.6	1.1	8.6	2.0	7.2	0.9
9	7.2	9.0	9.1	1.0	2.0	1.5	44	22	7.6	1.1	8.7	2.0		
10		8.7	8.5						7.5	1.1	8.5	1.2	6.4	0.9
11	6.6	7.2	8.6	>3.0	>3.0	3.0	44	22	7.4	1.1	9.0	2.0		
10-13														
14	6.9	9.0	8.8	3.0	1.7	1.2	44	19	5.5	0.83	8.4	1.5		
15		8.0	8.2						5.4	0.80	9.3	1.5	5.9	1.4
16	6.9	8.8	8.6	1.7	1.7	1.5	44	20	5.4	0.81	9.1	1.5		
17		8.7	8.4						5.4	0.80	9.0	1.0	5.5	0.5
18	6.9	7.7	8.5	2.8	1.9	1.6	43	24	5.3	0.81	8.6	1.5		
19		9.6	8.9						5.4	0.80	8.9	1.5	5.9	0.4
19	6.9	8.9	8.9	2.8	2.0	2.0	43	20	5.4	0.80	8.8	1.0		

(continued)

(continued)

TABLE 22 (concluded)

PLANT NO. 2										PLANT NO. 1				
DATE (1979)	pH			Free residual Chlorine (mg/L)			Chemical feed rate				Filter Effluent		Cl Feed	
	2	5	6	2	5	6	Alum (mg/L)	Lime (mg/L)	Chlorine pump sta.	Chlorine	pH	Cl Res.	a	b
										(mg/L)				
10-20	6.7	9.3	9.0	3.5	1.7	1.7	44	22	5.4	0.80	9.4	1.2	6.0	0.9
22		9.1	8.7						5.4	0.80	9.4	0.8		
23	6.7	8.1	8.4	2.5	1.8	1.5	46	24	5.4	0.81	9.3	1.0	5.6	0.8
24		9.6	9.1						5.4	0.80	9.3	1.0		
25	7.0	9.4	9.2	2.0	2.5	2.0	44	22	5.4	0.82	8.9	1.6	6.2	0.7
26		9.5	9.4						5.4	0.80	9.3	1.0		
27	7.0	9.1	9.3	3.5	1.0	0.9	43	24	5.2	0.78	9.0	1.6		
28														
10-30	7.2	9.4	9.4	0.1	0.7	0.8	43	24	0	2.0	9.3	2.0	4.9	0.8
31		9.4	9.1						0	1.9	9.3	2.0		
11-1	7.2	8.8	8.7	0	1.5	0.8	53	22	0	1.6	9.5	1.8	3.7	1.4
2		8.8	9.3						0	1.7	9.3	1.2		
3	7.2	6.9	7.8	0	1.5	1.0	60	22	0	1.8	9.4	0.7	4.0	1.1
4		9.0	8.8						0	1.8	9.0	1.8		
5	7.0	9.3	9.5	0	1.7	1.5	5.4	27	0	1.6	9.5	1.0		

a pre-chlorination (mg/L)

b pre-filter chlorination (mg/L)

Results

An examination of the data tabulated in Table 23 shows that Inst THM values in Amiss Plant No. 2 at sample site 2 (flume) were quite high, the result of rapid THM formation upon prechlorination. Data for weeks 1, 2 and 3 show that approximately 60% of the Inst THM leaving the plant were formed as a result of prechlorination. In week 1 vs. week 2, there was some lowering in Inst THM levels as a result of the fact prechlorine dose was lowered from 7.5 to 5.4 mg/L. However, the effect was probably due in part to lowering of incoming precursor levels, presumably due to a seasonal change in the lake. As a percentage of TERM-THM, INST THM levels in week 2 were hardly different from week 1 (32% vs. 34%).

Comparison of the data in Table 23 at site 6 for weeks 2 and 3 indicated no significant change in INST THM or TERM-THM levels as a result of the pH rise from week 2 to week 3, although again a change in raw water may have masked a minor effect.

Data for weeks 4, 5 and 6 showed an expected drop in INST THM levels as a result of the termination of prechlorination. Levels at site 2 (flume) did not go to zero, however, because of slow flushing of a reservoir at the pump station after the prechlorination point.

Values of THM Formation Potential are plotted in the bar graph figure 72. Superimposed are INST-THM values for the same period. This graph dramatically illustrates the overall detrimental effects of prechlorination in THM control at the Shreveport plant. Note during all four weeks the THMFP levels at sites 4 - 6 were about the same, while INST-THM levels were much higher while prechlorination was practiced (week three). Since THMFP reflects additional THM formation potential in the distribution system, the conclusion to be reached is as follows: the elimination of prechlorination does not simply defer THM formation to a later point in the treatment or distribution process. Rather, prechlorination apparently acts quickly to convert to THM's some precursor which would have been partially removed by flocculation/sedimentation. Whether this rapid reacting precursor is of a difference chemical type than other, slower acting precursors is not known. However, studies of ozonation of these same waters show a rapid initial diminution of THMFP, suggesting again the presence of a strong electrophile in the natural organic matrix (29).

Other Work Completed

Beginning June 3, 1980, five points located in the distribution system served by the Amiss plants were sampled weekly for Inst THM and TOC. These points were subjected to increased microbiological testing by the Amiss plant laboratory personnel. Additionally 6 sample points in Amiss Plant No. 2 were monitored for Inst THM and Term THM. This data was collected in anticipation of conversion of the Amiss plants to chloramination with continued weekly monitoring to enable a comparison of the two oxidants.

Due to problems with equipment, chemical feed rate control, and ammonia feed capacity the Amiss plants had not operated with chloramination

TABLE 23. SUMMARY OF INST-THM AND TERM-THM VALUES AT POINTS IN AMISS
PLANT - pH AND CHLORINE CONTROL EXPERIMENTS
(PHASES II B1 AND II B3)

WEEKLY AVG. (w/WEEKLY STD. DEV., N=4)

WEEK	SAMPLE POINT	TERM-TTHM	INST-TTHM	TTHMFP	NOTES
1	2	311(35)	107(25)	204	pH 8.8 Pre-Chlor. 7.5
2		275(20)	87(21)	188	pH 8.9 Pre-Chlor. 5.4
3		237(20)	58(23)	179	pH 9.3 Pre-Chlor. 5.4
4		210(28)	19(7)	190	Pre-Chlor. Terminated
5		134(4)	6.8(.4)	127	"
6		143(1)	9.2(.9)	134	"
1	3	277(5)	99(5)	178	
2		202(17)	72(5)	130	
3		167(15)	56(5)	111	
4		123(5)	12(1)	111	
5		86(1)	7.5(.1)	78	
6		100(5)	3.6(.2)	96	
1	4	288(25)	145(7)	143	
2		221(6)	98(12)	123	
3		202(16)	107(5)	95	
4		130(4)	16(3)	114	
5		97	10.6(.5)	86	
6		101	10.7(.1)	90	
1	5	276(30)	149(17)	127	
2		226(6)	110(3)	116	
3		204(17)	110(12)	94	
4		129(11)	33(11)	96	
5		102(1)	33(1)	69	
6		109(5)	31(9)	78	

(continued)

TABLE 23 (concluded)

WEEK	SAMPLE POINT	TERM-TTHM	INST-TTHM	TTHMFP	NOTES
1	6	298(15)	157(9)	141	
2		228(13)	115(9)	113	
3		207(12)	123(8)	84	
4		128(13)	43(7)	85	
5		111(2)	26(8)	85	
6		98(8)	36(.6)	62	
1	X (filter bottom Plant 1)	301(27)	157(26)	144	
2		242(11)	141(10)	101	
3		211(18)	140(15)	71	
4		192(10)	116(26)	76	
5		154(6)	83(2)	71	
6		150(1)	84(5)	66	

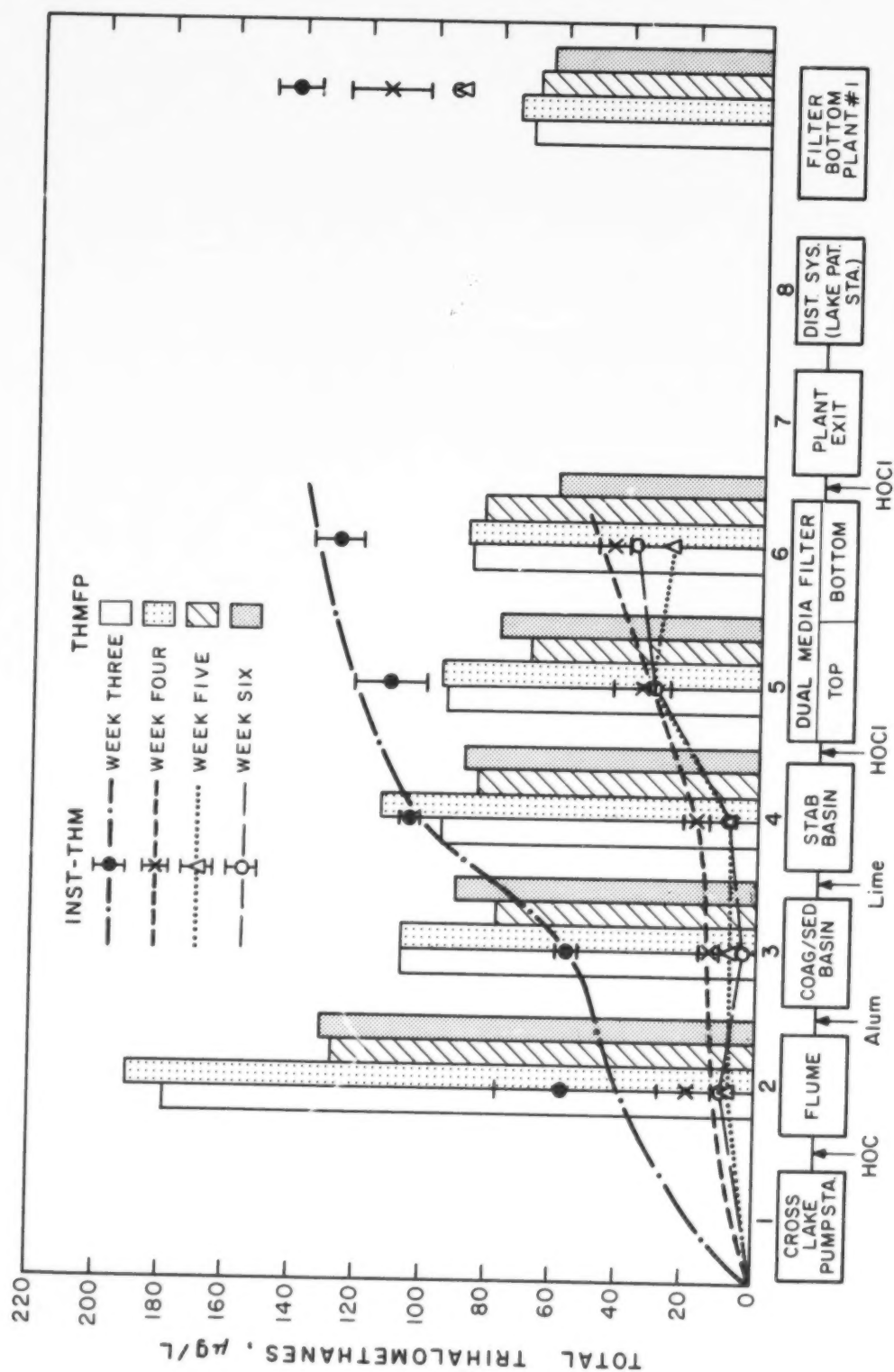


Figure 72. **THOMAS L. AMISS WATER TREATMENT PLANT #2**
 Instantaneous TTHM and TTHM Formation Potential Values in the
 T.L. Amiss Plant No. 2 during Process Modification Studies.
 Prechlorination Eliminated Week 4.

for a significant continuous period of time when sampling was ended in August 1981. Results of chloramination's effect on THM formation in the Amiss plants may be reported at a later time.

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